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THE

PHYSICAL REVIEW.

A CRITIQUE AND STUDY ON THE NATURE OF THE VOLTA EFFECT.

BY ALBERT E. HENNINGS.

FOR over a century, physicists have diligently sought an explanation of the Volta effect. Although numerous and extensive investigations have been undertaken for that purpose, no general agreement has yet been reached. This is due in part to the difficulties and uncertainties inherent in the problem which extend even to the simplest experiments. It is a matter of importance, therefore, that simple and crucial experiments be devised and that they be performed in such a way as to yield results which are incontestable. Not before is it permissible to attempt "explanations." Hence the primary object of this paper is to establish more firmly some of the significant facts rather than to advocate vigorously any theory in regard to the fundamental nature of the Volta effect.

EXAMINATION OF SANFORD'S RESULTS.

A recent article[1] by Sanford makes such a study not untimely. He has described experiments the results of which, as he interprets them, furnish an effective argument against the so-called electrolytic theory of the Volta effect. He believes he has shown that the charge exhibited by an insulated conductor, such as a ball, after it has made contact with the *inner* surface of a hollow earthed conductor, such as a beaker, is dependent on the nature of the *outside* surface of the latter. This conclusion, upon which his argument is chiefly based, seemed untenable to the writer because the generally accepted facts of the phenomenon, together with incidental observations in an investigation now going on in this same field, left no doubt in his mind that the Volta effect depends *solely* upon the nature of the *opposed* surfaces. (By opposed surfaces is meant the two metal surfaces which, with the intervening dielectric, constitute the condenser system, the charge upon which is measured in experiments upon the Volta effect.)

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[1] PHYS. REV., XXXV., p. 484, December, 1912.

An attempt was therefore made to reproduce the essential elements of the experiment described by Sanford. The whole assemblage of apparatus was enclosed in a cage of wire netting however and a Dolazelek electrometer was used instead of an electroscope. While the results obtained were fairly consistent for observations taken consecutively there were large and apparently unaccountable variations from one time to another. After making several series of unsatisfactory observations, it was discovered that the silk cord which in Sanford's experiments served to insulate the ball and to raise or to lower it was invariably charged. Decided induction effects were therefore produced which could not be eliminated even when the ball was attached by a wire so that no part of the cord came within 20 or 25 cm. of any portion of the beaker. All the cases described by Sanford were investigated several times but none yielded results which could be interpreted as Sanford interpreted his. In spite of the disturbing influence of the charged cord, there seemed to be no doubt that the Volta effect depended on the opposing surfaces. It is certain that in Sanford's experiments, the true effect was masked to a large extent by disturbing causes. An insulating silk cord absolutely devoid of an electrical charge appears to be an impossibility. And when it is noted that the arrangement is then an ideal one for charging by induction it is obvious that the charge exhibited by the ball would depend to an indeterminable extent on the intensity and orientation of that on the cord.

A. MODIFICATION OF THE EXPERIMENTAL ARRANGEMENT: QUALITATIVE MEASUREMENTS.

In order to do away with the silk cord and the attendant disturbances, it was decided to insulate the metallic beaker instead of the ball and to operate the ball with an earthed wire. It was decided also to study a larger number of cases than had been investigated by Sanford.

It was found that pieces of sealing wax did not serve satisfactorily for insulating the discs and beakers which were to be used because leaks and noticeable charges very soon developed. An insulating stand was then constructed of small tubes and narrow strips of brass with a portion of the legs made up of slender ebonite rods. The apparatus was disposed as shown in Fig. 1, all being enclosed in a wire cage which was well grounded. All manipulations took place from the outside.

The sensitiveness of the electrometer needle was such that when charged to about 30 volts a potential difference of one volt between the pairs of quadrants caused the reflected image from the mirror attached to it to move 140 mm. at a distance of 125 cm. The conductor to be examined was placed upon the insulating stand and the ball lowered to contact. The grounding key, K_1, was raised by a lever whose fulcrum was at f_1. Then the ball was made to rise so far above the insulated body

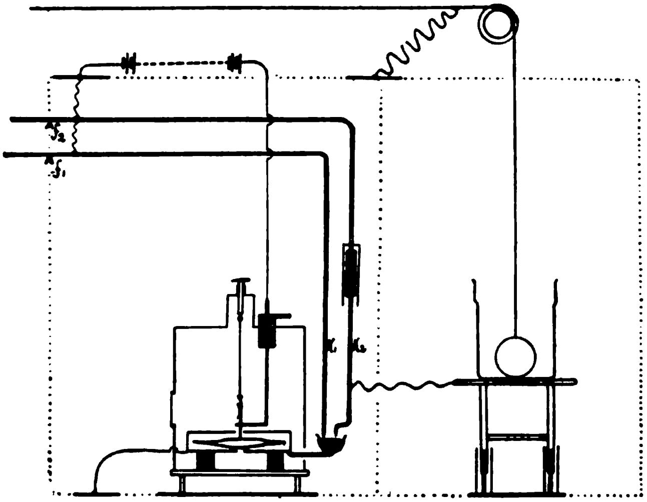

Fig. 1.

as to have no further influence upon it. This charge was divided with the insulated quadrants of the electrometer by bringing K_2 into the mercury cup. Then K_2 was raised, the ball lowered and raised, and K_2 again lowered in turn. These successive operations were repeated until the electrometer needle indicated practically no further increase in the charge on the insulated pair of quadrants. The latter were then at approximately the same potential as the insulated body. This method was used merely in order to conform as nearly as possible to Sanford's procedure. The keys, K_1 and K_2, as well as the wire attached to the ball were manipulated from the point at which observations were made. The potential indicated by the electrometer would of course not be the potential difference actually existing between the opposing surfaces at the time of contact. Nor indeed can the Volta P.D. be found with this sort of an experimental arrangement since the capacity of the system consisting of the ball and beaker or ball and disc cannot be evaluated. Comparisons may be made, however, between results obtained under the same conditions and definite conclusions drawn from them.

The ball was one of steel, 5 cm. diameter. Discs of brass and aluminum as well as beakers of these metals were used as the insulated conductor.

These were also covered in various degree with tinfoil. The discs were each 9 cm. in diameter. The brass beaker was 10 cm. in diameter and 12.5 cm. high and the aluminum beaker was 10 cm. in diameter and 14.5 cm. high.

With the above arrangement, series of results obtained at intervals extending over days were in such excellent agreement that disturbing influences must have been quite removed. Such differences as did appear were no larger than could be accounted for by the probable errors of observation in this simple and comparatively crude method of procedure. Changes with time are also to be expected because of the variable surface condition of the conductors. The numbers given in connection with each of the several cases to be described are the means of three values obtained in as many complete series of observations taken on different, not consecutive, days. They represent in volts the approximate maximum potential indicated by the electrometer in the manner outlined above when the steel ball had been in contact with the particular body under the conditions to be specified. The order of accuracy of the individual observations from which the means are taken lay within .02 volt.

With the ball making contact with the center of the brass disc, the observed values were

−.093 volt for one face,
+.027 volt for the other face.

This indicates merely a dissimilarity between the two faces. When one of the faces was completely covered with tinfoil the value was

+.403 volt for the tinfoil surface,

and when a circular hole 2.5 cm. in diameter was cut in the tinfoil thus allowing the ball to make contact with the brass without touching the tinfoil the value became

+.023 volt for the first of the two faces considered above in the presence of the tinfoil ring,
+.107 volt for the other face considered above in the presence of the tinfoil ring.

The tinfoil has thus a marked influence upon the result although the ball does not make contact with it. Similarly with one face of the aluminum disc the observations gave

+.690 volt for the naked disc,
+.400 volt for the tinfoil surface,
+.633 volt for the face covered with tinfoil except for circular space 2.5 cm. in diameter in the center.

Again the tinfoil makes its presence felt. In both cases the change which it brings about is such as to bring the combined effect toward that observed for it alone and indeed the amount of this change is the greater the larger the difference between the independent effects of the tinfoil and the metal upon which it is placed.

When the discs were replaced by the beakers in an upright position so that the ball made contact with the center of the bottom on the inside, the observed values were

−.103 volt for the brass beaker,
+.390 volt for the aluminum beaker.

Upon placing cylinders of tinfoil on the inside of the beakers leaving the bottoms exposed, the values became

+.047 volt for the brass beaker,
+.357 volt for the aluminum beaker.

The change brought about by the tinfoil is surprisingly great when it is noted that the portion of its surface nearest the ball was over 2 cm. away. The extent of the surfaces opposed to, and within range of each other, was very large however.

When the outside of the beakers was covered with tinfoil, leaving exposed the inside surfaces, the values observed, after the ball had been brought in contact with the bottom, were

−.100 volt for the brass beaker,
+.380 volt for the aluminum beaker.

These values are the same as those obtained with the naked beakers. The effect is, therefore, *completely independent* of the nature of the *outside* surface.

This last conclusion was confirmed by using what was in effect a hollow vessel with a brass bottom and tinfoil sides. The brass disc was placed in the bottom of the beaker, the sides of which were covered with the tinfoil cylinder used above. The ball then made contact with the center of the disc. This gave

+.093 volt with brass on the outside,
+.080 volt with aluminum on the outside.

Replacing the brass disc by the aluminum disc gave

+.477 volt with brass on the outside,
+.467 volt with aluminum on the outside.

Evidence that the effect is independent of the outside surface is not wanting. (That the values for the aluminum beaker should tend to be somewhat less than those for the brass beaker in these cases, is accounted for by the fact that, since the aluminum beaker is larger than the one of brass, the capacity of the insulated system is slightly greater with the former than with the latter, forming a part of it.)

When the brass disc was placed on the bottom of the inverted beakers with the ball making contact with the center of the disc, the observed values were

−.067 volt with brass disc on brass beaker,
−.060 volt with brass disc on aluminum beaker.

With the aluminum disc replacing the one of brass, the values were

+.403 volt with aluminum disc on brass beaker,
+.390 volt with aluminum disc on aluminum beaker.

It is here seen that the effect depends only on the opposing surfaces, as has been apparent in all the preceding cases.

These several cases were varied by using also a brass ball, and a number of other special cases were studied but the results are not here presented since they are in every respect similar to those given above. They all furnish unmistakable evidence that the Volta effect depends *only* on the nature of the *opposing* surfaces. By none of the results is there suggested any argument in favor of the possibility that the effect depends even in the slightest degree on the nature of the surface of the outside of a hollow conductor when a second conductor has made contact with the inside. It is only those portions of the surfaces which are exposed to, and within range of, each other that come into play. All such surfaces contribute to the general effect according to their extent and relative proximity.

It is to be noted, as stated before, that the numerical results which have been given do not represent the true values of the Volta P.D. Also, since the capacity and relative proximity and extent of the opposing parts are not the same in all cases, the deviations vary accordingly. Thus, the effect observed between the ball and the aluminum plate is apparently greater when the latter is examined alone than when it is placed upon the bottom of an inverted beaker. The real effect is the same for both but does not appear so because the capacity of the insulated system is greater in the one case than in the other. However, except for the aluminum beaker being somewhat larger than the one of brass, the conditions and circumstances surrounding those cases which furnished the arguments for any of the general conclusions were similar in all respects. Hence the conclusions which have thus far been drawn are the inevitable ones which would be reached through a knowledge of the exact values of the Volta P.D.'s.

It is obvious that the surfaces of different conductors in connection with the earth, either separately or in mutual contact, are at different yet definite potentials with reference to the earth and thus exhibit definite potential differences with reference to each other. It must be assumed that the entire surface of a conductor in air is a seat of electrification the nature and intensity of which is characteristic of the surface. If the conductor is composed of dissimilar metals or if its surface is non-homogeneous, then the intensity and character of the electrification displayed in various portions of the surface are variable and fluctuate in such a way as to reflect accurately the conditions in the region considered.

B. A CLOSER STUDY OF THE PHENOMENON: "APPROACH" AND "SEPARATION" CHARGES.

A more detailed study of a few of the cases was found desirable and of service in extending and confirming the interpretations already given. The experiment was accordingly modified in this way: The conductor to be examined was permanently connected with the electrometer by means of the key, K_2 (Fig. 1). After bringing the ball in contact with the conductor on the stand and raising K_1, the grounding key, the ball was *very slowly* raised and the deflection of the electrometer needle noted as the ball moved upward.

With a brass plate, there was a deflection of 6 mm. to the left just as the ball began to rise which became greater as the ball rose higher, reaching a maximum of 12 mm. when the lower extremity of the ball was 5 or 6 cm. from the disc. As would be anticipated from the above, there was a deflection to the right when the ball approached the plate if the latter had been first earthed and then insulated. Furthermore when the ball moved away from a point *near*, instead of in contact with, the surface of the plate which had been discharged to earth and then insulated, the deflection was of course to the *left*. The deflection to the right indicated a positive, that to the left, a negative, charge. These have been termed by Majorana[1] "*approach*" and "*separation*" charges respectively. These phenomena, if no others, make it necessary to assume that, whatever be the fundamental cause of the electrical manifestations at the surface of a conductor, they deport themselves just as would an insulated electrical layer of uniform (for a given conductor of homogeneous surface) distribution. It is under the limitations of this assumption that the surface of conductors will be spoken of as being *charged*. The surface of the ball being thus positively charged with reference to that of the brass plate induces a relatively negative charge in the latter upon approaching it, and a positive charge in the quadrants of the electrometer.

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[1] Phil. Mag., XLVIII., p. 241, 1899.

When the ball moves away the charges that were induced are redistributed. With the aluminum disc the approach and separation charges due to the ball were larger and of opposite sign to those noted for the brass, the aluminum being positive with reference to the steel ball.

In the case of the brass disc covered with tinfoil except for a circular space in the center, it was found that while the deflection of the electrometer needle was 7 mm. to the right when the ball was far removed, it was to the left just as the ball began to rise, reaching a maximum in that direction when the ball was about 2 or 3 mm. away. Then as the ball continued upward it shifted to the right. This is to be explained as follows: While the brass is negative, the tinfoil is positive, with reference to the ball. Accordingly, a relatively negative charge is induced in the brass, and a relatively positive charge is induced in the tinfoil. When the ball is completely removed these charges become free, the resultant charge indicated being of the sign of the greater. A negative deflection is first indicated because for the first 2 or 3 mm. the charge induced by the ball in the brass is released at a greater rate than that induced in the tinfoil. Then the relative change in induction between the ball and the tinfoil becomes the greater. The final charge displayed is the net result of all the factors at work just as the ball leaves the point of contact. It is seen to some extent how the individual factors contribute.

A brass beaker was examined in the manner outlined above, first naked and then with a tinfoil band about 3 cm. wide covering the upper inside portion. Fig. 2 shows the various approximate positions of the ball at which the deflections of the electrometer were noted together with the corresponding magnitudes of these deflections in millimeters. The fact that the end results were the same for both indicates that when the

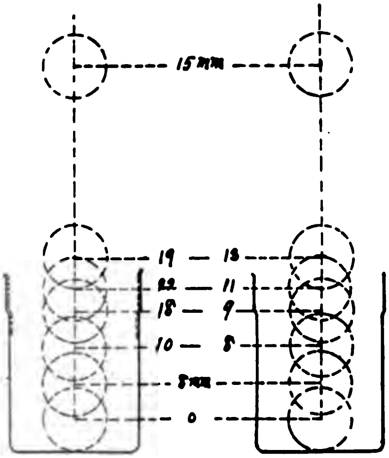

Fig. 2.

ball was in the bottom of the beaker the tinfoil was too far away to exert any influence. It was found that this continued to be the case when the beaker was covered half way down on the inside with tinfoil. When extended beyond this point, the tinfoil began to make its influence felt. It is seen that the deflection which was in the negative direction showed a temporary increase as the ball approached and passed by the tinfoil collar. Considering the brass beaker alone, the increasing deflection is due to the separation charge between the ball and the beaker. With the tinfoil present there are successively an approach, and a separation, charge due to the tinfoil and the ball. These are simply superimposed upon the separation charge due to the ball and the beaker. A "tinned" surface in place of the tinfoil produced an effect of approximately the same magnitude. A band of copper wire gauze on the inside of an aluminum beaker produced a similar effect, the deflections being in the positive direction since the aluminum was positive, and the gauze negative, with reference to the ball.

This minute study of the approach and separation charges thus furnishes an excellent means of analyzing the effects of composite surfaces. Each portion acts independently, its contribution to the general effect being just what it would be if it acted alone, so that taking into account the disposition and extent of the components, the estimated effect coincides with that observed.

C. Quantitative Measurements of the Volta Effect with Composite Surfaces.

While the above experiments serve admirably to establish general relationships, they are not adapted for exact quantitative measurements. To decide whether the components of a composite surface contribute to the general effect in *exact* proportion to their extent, their relative proximity, and the intensity and character of their electrification required another experimental arrangement.

Suppose we have two plates, A and B, with their faces parallel and near, but not in contact with, each other. Let A be connected to one pair of quadrants of an electrometer which together with B are grounded. Then upon insulating the quadrants with which A is in communication and moving B away, a separation charge is noted by means of the electrometer because of a characteristic difference of potential between the surfaces of A and B. The plate B may be so charged with a potential divider that there will be no deflection set up in the electrometer upon moving B either away from, or toward, A. The potential thus applied to bring this about is simply superimposed upon the surface potential already existing so that it is numerically equal, and opposite in sign, to the original P.D. between the surfaces of *A* and *B*. Direct "contact" is not made between the surfaces; they are merely in temporary communication through the earth. This is one of the familiar methods of measuring the Volta P.D. between two given metals. The foregoing results suggest the hypothesis that if the surface of *A* be made up of two or more metals then the compensating potential will be the *average* P.D. between *B* and the constituent parts of *A*. It was to ascertain if this is a fact that the following experiments were made.

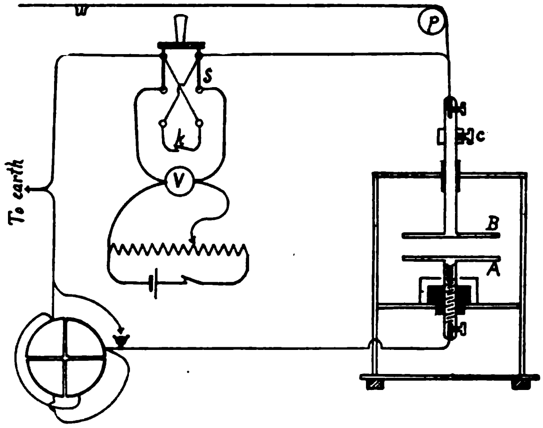

Fig. 3.

The arrangement is sketched in Fig. 3. *A* is the insulated plate which was removable, one of brass and one of aluminum being used. Each was tested against *B*, a brass plate, both naked and covered in various proportions with tinfoil. The insulating plug consisting of ebonite was covered with a metal cap to screen off disturbances likely to arise from possible charges on its surface. The initial distance between *A* and *B* was roughly adjusted by the set-collar *c*, and then more accurately by screwing *A* up or down in the insulating plug. When *c* rested upon the projecting sleeve of the upper portion of the brass frame, *A* and *B* were at a fixed minimum distance apart. The plate *B* was raised or lowered by means of the wire *w* operating over the pulley *p*. *B* and the frame were charged by means of a potential divider. The reversing switch *S* made it convenient to charge either positively or negatively and *k* served to ground the system. The functions of the other parts of the apparatus suggest themselves. The electrometer and the frame supporting the plates were enclosed in the wire cage of the preceding experiments.

In the actual experiment it was not wholly satisfactory to adjust the compensating potential until a balance was reached since the sensitiveness of the arrangement was greater than the accuracy with which the readings on the voltmeter could be made. Therefore the P.D. across the terminals of the voltmeter was fixed at some convenient value. The method was then to apply this P.D. positively and negatively in turn to *B*, noting in each case the deflection in the electrometer upon raising *B*. Proceeding in this way we have:

$$E = PD\frac{d_1 + d_2}{d_1 - d_2},$$

where

E = natural P.D. (*i. e.*, the Volta P.D.) between the surfaces.
PD = applied P.D.
d_1 = deflection of electrometer when $+PD$ is applied to *B*.
d_2 = deflection when $-PD$ is applied.

d_1 and d_2 are to be taken with their sign, the balancing point of the needle being zero.

The plates were 8 cm. in diameter and the initial distance between their surfaces was 1.75 mm. The tinfoil covering the surface of *A* in whole or in part was of course nearer. It was smoothed out by pressing it with a similar piece of foil covering the fingers. Its upper surface was estimated to be on the average approximately .25 mm. above that of the plate beneath. The fact of its being nearer to the opposing surface than that of those exposed portions of the surface upon which it is placed will involve a correction which will be taken up later.

In the table which follows are given a sample series of results. The plate was first examined entirely covered with tinfoil. Then a sector of 120° of the tinfoil was removed, followed by 60°, 60°, 120° more successively so that the final test was with the naked plate. The latter part of the table gives the results with the surfaces divided concentrically, *i. e.*, a circle of one half the area of the plate was cut out of the foil exactly covering it. Measurements were made with the ring of foil as well as with the small circle which had been cut out, each being centrally placed upon *A*.

The calculation of the average P.D. which exists between a homogeneous surface *B*, and a composite surface *A*, is made as follows:

Suppose the dissimilar surface to consist of two metals, each of which is homogeneous, and in the same plane, then

$$E = \frac{a_1e_1 + a_2e_2}{a_1 + a_2},$$

where

E is the average P.D. between *A* and *B*.
e_1 is the P.D. between *B* and one of the parts of *A*.

a_1 is the area of this part of A.
e_2 is the P.D. between B and other portion of A.
a_2 is the area of this portion of A.

Ratio of Exposed Surfaces.		P.D. Observed.	P.D. Calc. Supposing Surfaces in Same Plane.	P.D. Corrected by Reducing Surfaces to Same Plane.
Surfaces divided radially				
Tinfoil	Aluminum			
1	0	+.352	.352	.352
2	1	.472	.483	.469
1	1	.530	.548	.533
1	2	.597	.614	.600
0	1	.744	.744	.744
Tinfoil	Brass			
1	0	+.336	.336	.336
2	1	.237	.225	.236
1	1	.184	.169	.182
1	2	.118	.113	.125
0	1	.002	.002	.002
Surfaces divided concentrically				
Tinfoil	Aluminum			
1	0	+.366	.366	.366
1	1			
Aluminum outside		.549	.560	.544
Aluminum inside		.539	.560	.544
0	1	.754	.754	.754
Tinfoil	Brass			
1	0	+.380	.380	.380
1	1			
Brass outside		.207	.192	.206
Brass inside		.214	.192	.206
0	1	.004	.004	.004

If the parts of the dissimilar surface are not in the same plane, the portion which is the closer contributes relatively as much more to the general effect as it would if its surface were larger in the ratio by which it is the nearer to the opposing surface. The above expression must then be rewritten in the form,

$$E = \frac{a_1 e_1 + a_2\left(1 + \frac{d_1 - d_2}{d_2}\right) e_2}{a_1 + a_2\left(1 + \frac{d_1 - d_2}{d_2}\right)},$$

where

d_1 is the distance between B and portion a_1 of A.
d_2 is the distance between B and portion a_2 of A.

Upon applying this correction it is seen that the agreement between the observed and calculated values as shown by the first and third columns of the table is as close as the limits of the accuracy of the measurements permit. In the case of the surfaces being divided concentrically it appears that the portion exposed in the form of a ring contributes more than an equal portion in the form of a circle in the center. This is accounted for by the fact that the effect due to the edges of the opposing surfaces is not negligible so that the effective surfaces are slightly greater in extent than the dimensions indicate. This increment accrues to the advantage of the outer ring.

A composite surface of brass and lead was formed by pressing brass gauze into a sheet of lead by means of a roller press. The lead coming through the openings was pressed flat but left exposed one face of the brass gauze. The strands of the latter were also flattened at their crossing points so that the whole surface was approximately plane. The lead alone when passed through the press showed a P.D. of +.37 volt against the brass plate, and the gauze similarly passed through gave −.13 volt. The gauze and lead together gave +.14 volt. Since the gauze was made up of wire .55 mm. in diameter, 12 strands to the inch, the ratio between the exposed surfaces of lead and brass was approximately 52 to 48. The computed average P.D. between the brass plate and this composite surface was thus +.13 volt which compares favorably with +.14 volt, the observed value.

A piece of very fine copper gauze of 45 strands to the inch was almost completely imbedded in a sheet of lead by pressing it well in and then burnishing with a convex-faced steel tool, leaving the copper exposed only at the crests formed by the crossing strands. The ratio between the exposed copper and lead surfaces as estimated by examining under the microscope was 7 to 93. While the measured P.D.'s against the brass plate were −.20 volt and +.37 volt for the gauze and lead respectively, that for the combined surface was +.34 volt, as compared with +.33 volt, the theoretical value.

It is unnecessary to produce further evidence that the Volta effect observed for a composite surface may be determined by considering the independent effects of the constituent parts of this surface.

D. The "Screening" of the Volta Effect with Wire Gauzes.

The question as to what extent a metal plate will contribute to the effect through a perforated sheet placed upon it was suggested by the foregoing experiments. A qualitative study of this point was made by placing gauzes of different meshes upon the brass and aluminum plates. The latter having shown P.D.'s of +.004 volt and +.754 volt respectively against the movable brass plate, would, to the extent that they were effective through the gauze, produce a difference in the observed P.D. when a given sheet of gauze was placed upon each in turn. The pieces of gauze were cut slightly larger than the plates upon which they were placed to preclude the possibility of the edge effects of the latter, and were smoothed out so as to conform as nearly as possible to a plane. The distance between the plates was kept at 2.5 mm. so long as this distance was two times, or more, that between the upper surface of the gauze and that of the plate beneath, being increased however when the coarser gauzes were used so as to make this ratio about 2 to 1. Proceeding in this manner the following results were obtained, as the means of three observations in each case.

Kind of Gauze.	No. of Strands to Inch.	Diameter of Strands in Mm.	P.D. Observed on Aluminum.	P.D. Observed on Brass.
Copper............	45	.15	−.202	−.203
Brass.............	30	.25	−.259	−.260
Brass.............	16	.45	−.208	−.210
Brass.............	12	.55	−.249	−.256
Brass.............	6	.75	−.168	−.111
Brass.............	16/3	.45	+.033	−.106

Not until there are 12 strands to the inch is there an effect through the gauze which is decisive. The differences up to that point are no greater than the probable errors of observation. Indeed the observed effect is practically that which we would have with the gauzes alone until the size of the holes is equal to or greater than their depth. For the finer gauzes the average depth of the holes was about 2½ times, perhaps more for the finest one, the diameter of the strands, because the gauze could not be made to lie perfectly smoothly upon the plates. As the ratio between the size and depth of the holes grows, the plate beneath becomes increasingly effective through them.

Perhaps the only way to study this point in a really quantitative fashion would be to have two metals made up in the form of square rods and arranged on the order of a thermopile, each set rigidly connected together and movable along their axes. A plane surface consisting of the two metals could be formed of the ends of the rods by proper adjustment. Then by moving one set of rods one way or the other, holes of varying depth could be obtained with either metal in the foreground. In order to have holes of different sizes, would of course require rods of corresponding dimensions. An experiment of this kind will be necessary to determine whether, upon taking proper account of the relative extent and distances of the surfaces of the two metals (including the sides of the holes) with reference to an opposed surface, the simple considerations outlined above for composite surfaces will lead to results which are related in some exact way to those observed.

Summary.

The Volta effect depends, under *all* circumstances, on the nature of the *opposing* surfaces of conductors which have been brought near, or in contact with, each other. Indeed it depends *only* on the surfaces exposed to, and within range of, each other. All, and only, such surfaces, or portions of surfaces, of conductors contribute to the general effect. The results of experiments purporting to prove otherwise are spurious. Hence Sanford's chief argument against an electrolytic theory of the Volta effect fails because of a misapprehension in the premises.

The surfaces of conductors which have been discharged to earth act just as though they were definitely and characteristically charged. In the case of a homogeneous surface, this postulated electrification is uniformly distributed, while for a surface of dissimilar parts, its nature and intensity vary from part to part. The surfaces being the seat of such electrical manifestations exhibit, as a consequence, a definite P.D., the so-called E.M.F. of contact, between each other. It is only in terms of these potential differences that the phenomenon lends itself to quantitative treatment.

The effect observed with composite surfaces has been shown to be the *average* effect of the constituent parts, each of which contributes in *exact* proportion to its extent, its relative proximity, and its own P.D. with reference to the opposing surface.

The effect is practically completely "screened" when the lateral dimensions of the openings in the screen are not greater than their depth. An increase in the ratio from unity upward between the width and depth of the holes results in an increasing effect through the openings.

Taken as a whole, the results show that the phenomenon has its seat in the surface. The fundamental question, then, reduces to one in regard to the actual conditions on the surface of a conductor. Is there an insulated electric layer brought into existence by chemical or other means, or are the manifestations due to intrinsic properties of the conductor which make themselves felt at its boundaries? This question is still an open one so far as the present investigation goes.

The facilities for this study were afforded at the Ryerson Physical Laboratory. The writer takes this opportunity to thank Professor Millikan, whose unfailing interest in the work has been a source of inspiration.

The University of Chicago,
March, 1913.

THE TRANSMISSION OF CANAL RAYS THROUGH THIN PARTITIONS.

BY ALFRED N. GOLDSMITH.

I. INTRODUCTION.

THE canal rays were discovered by Goldstein in 1886, and through the researches of W. Wien in 1898, and later of Sir J. J. Thomson, their identity with the positive ions was definitely established. They have been frequently employed since as a source of positive ions for investigation of the properties of positive electricity.

The mode of production of the canal rays involves the use of a perforated cathode in a tube containing a gas at low pressure through which an electric discharge is passing. Back of the perforation in the cathode will be found a column of rapidly moving positive ions, their presence being detectable by the fluorescent, photographic, and electrostatic effects which they can produce. J. Stark[1] discovered the Doppler effect which is displayed by the canal rays behind the cathode, as evidenced by the shift of the lines of the spectrum when viewed respectively in directions perpendicular and parallel to the direction of motion of the ions. His experiments showed that the velocity of the positive ions was the same as the velocity of the ions when measured by means of the "magnetic and electric spectra." The magnetic and electric spectra are obtained when the ions pass through strong electric and magnetic fields. From the observation of the resulting deflections of the beam of canal rays it is possible to evaluate e/m and v.

In 1907 Thomson[2] showed, by examination of the magnetic spectrum obtained in gases which had been as carefully as possible freed from all traces of hydrogen that the value of e/m for some of the positive ions was $(10)^4$, $5(10)^3$ and $2.5(10)^3$. The two former values correspond to the hydrogen atom and molecule, and the latter to the helium atom. At lower pressures in all gases, positively charged atoms of hydrogen were found to be present in spite of the attempts at purification of the gas. W. Wien then called attention to his earlier hypotheses that the positive ions lose their positive charge, that is, are neutralized at some point of their path and then may be again positively electrified by the loss of negative electrons, and also that ions of larger mass than those usually found exist in the discharge. His conclusion,[1] that the hydrogen found in the discharge tube was present only as an impurity was disputed by J. J. Thomson,[2] who found that even when the amount of hydrogen was greatly changed, its presence did not become more prominent. He suggested later[3] that, reasoning from the constancy of the velocity of the canal and retrograde rays, they owe their velocity either to an explosion in the atom or their charge is different at different points of their path. Possibly both causes are operative. Wien's hypothesis of the existence of neutralized positive ions in the canal rays was shown to be well-founded by experiments undertaken by Thomson in 1908.[4]

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[1] Phys. Zeitschr., *6*, p. 892, 1905.

[2] Phil. Mag., p. 561, May, 1907.

W. Wien found,[5] reasoning from the experimentally determined magnetic deflections of the positive ions in the canal rays, that the greatest velocity they attained was that which would be given to a positively charged atom of the gas which owed its velocity to the potential gradient actually existing in the tube.

As early as 1903, J. Stark[6] had suggested that neutral doublets or even negatively charged canal rays might be produced, and that these, moving with high velocities, would cause effects similar to those produced by the positive ions.

O. Reichenheim[7] showed that in the canal rays in oxygen there are three kinds of ions prominently present, namely the hydrogen atom, the hydrogen molecule, and the oxygen atom. In general the spot of light in the magnetic spectrum corresponding to the hydrogen atom is the most evident. Similarly, the presence of the hydrogen atom in the cases where the tube was filled with argon or nitrogen was observed, though in these cases it was not easy to find the charged atoms of the gas filling the tube.

A research of Thomson[8] established the existence of three kinds of canal rays. Firstly, rays which are not deflected by electric or magnetic forces. Secondly, "secondary rays" which are produced by the collision of rays of the first kind with the molecules of the gas. Thirdly, rays which appear at low pressures, have velocities proportional to the difference of potential between the electrodes, and for which e/m is inversely proportional to the atomic weight of the gas in the tube. The secondary rays always have a velocity of $2(10)^8$ cm. per second and a value of e/m of 10^4. That their velocity is independent of the potential difference between the electrodes suggests that they may be produced by the dissociation of the molecules of the gas by a sort of trigger action, and their energy comes from the store of molecular energy originally present.

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[1] Phil. Mag., *14*, p. 212, 1907.

[2] Phil. Mag., *14*, p. 295, 1907.

[3] Phil. Mag., *14*, p. 359, 1907.

[4] Engineering, *85*, p. 518, 1908. Phil. Mag., *16*, p. 657, 1908.

[5] Ann. d. Physik. *27*, 5, p. 1025, 1908.

[6] Phys. Zeitschr., *4*, p. 581, 1903.

[7] Zeitschr. Elektrotech., *16*, pp. 583, 585, 1910.

[8] Phil. Mag., *20*, p. 752, 1910.

Certain properties of the α rays from radium are of interest and will be briefly considered. Bragg and Kleeman[1] first discussed the diminution of velocity of the α particles which was sufficient to cause them to lose their ionizing power. They found that the critical velocity was about $1.5(10)^9$ cm. per second. which is 60 per cent. of the initial velocity of the homogeneous rays from Radium C. It is quite possible that uncharged particles not electrically detectable can continue passing through matter even at the end of their so-called range, for it is a very improbable assumption that the velocity suddenly falls from the critical value to zero.

The most important work as to the actual nature of the α rays was done by Rutherford and Royds.[2] By passing the α particles through the walls of a thin glass chamber (0.01 mm. thick) into a space exhausted to a high vacuum and compressing the trapped gas in a tube where its spectrum could be examined, they succeeded in definitely proving that the α particle after losing its positive charge was helium. The spectrum of the helium gradually developed in the spectrum tube, in some cases taking as long as six days to become completely visible. Check experiments were performed to test for possible diffusion or leakage of the gas through the thin glass containing tube. The method of isolation of α rays by transmission through thin partitions, so successfully employed by Rutherford in this instance, was used in the present research into the nature of the canal rays.

II. OBJECT OF THE RESEARCH.

The following experiments are an attempt to pass the canal rays through a thin diaphragm into a highly vacuous separate chamber where the spectrum of the accumulated gas, if any, can be examined free from disturbances of the electric discharge which produced the canal rays.

III. DESCRIPTION OF THE APPARATUS.

The discharge tube used in the experiments is shown in Fig. 1. The anode is *A;* and *B*, a ring of aluminum with a large hole in its center is the cathode. The potentials used were at times so high that it was difficult to secure high insulation because of surface leakage over the glass. Therefore the terminal wires were run from the platinum leading-in wires at *S* and *P* to the points *T* and *Q* through glass tubes which were sealed in place and of which the ends were filled with sealing wax. Connection to the pumps was secured by a side tube at *F*. To prevent the canal rays striking the edge of the disc *U* (where the sealing cement was occasionally present) a guard ring was placed at *L*.

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[1] Phil. Mag., Dec., 1904.

[2] Chem. News, *99*, p. 49, 1909.

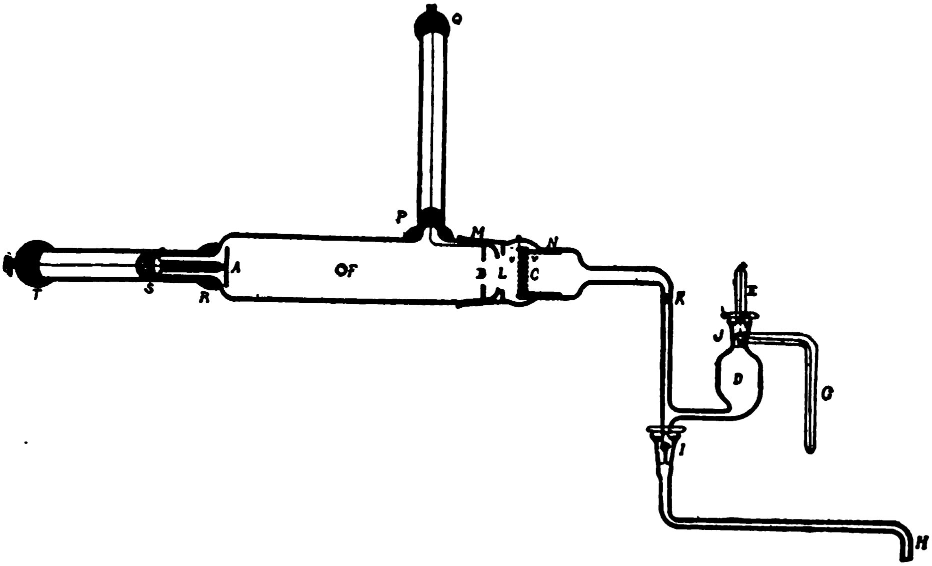

Fig. 1.

It was desirable at times to remove the plug *C* and the diaphragm carried therein without rebuilding the portion of the apparatus surrounding it, and this became possible by placing a ground joint at *M*. The thin partitition used in the experiments was carried on the front face of the steel plug *C*, this face being perforated with circular holes 1 mm. in diameter. The thin diaphragm, through which the canal rays passed, was sealed with cement on the front face of *C*. The cement was very carefully placed so that none of it was in the path of the moving ions. Over the diaphragm was fastened the plate *U*, which had in it holes coinciding in size and position with those in *V*. The plate *U* was screwed to *V* at the edges after cement had been placed on the back of *U* to fasten it gas-tight to the diaphragm. As before, the cement was carefully kept out of the path of the ions. The steel plug fits into place at *N*. In order to connect that portion of the apparatus which is back of the diaphragm to the vacuum pumps and outlet with a stop-cock was placed at K. Connection with a mercury reservoir was secured through the tube H, I is a mercury sealed stop-cock to the small discharge tube E, which is of fairly fine capillary tubing. Connected to E is G, a piece of the finest capillary tubing.

It will be seen that the vacuum apparatus is really two chambers, AB and CD, which are divided by the air-tight partition at U. This partition was thin enough to permit the penetration and passage of the positive rays. These particles at high velocities were thus passed from the chamber AB to the chamber CD, where they accumulated and were examined.

Experiments were tried in air, carbon dioxid, hydrogen, argon, and helium. The argon was prepared by sparking air in the presence of an excess of oxygen, which excess of oxygen was afterward removed by yellow phosphorus. Helium was produced with the same apparatus except that instead of starting with air, the gas obtained by heating monazite sand was used. Since this gas is a mixture of air and helium, it was not difficult to secure rapidly the necessary amount of helium.

Gaede and Geryk pumps permitted reaching and holding a vacuum of less than 0.0001 mm. in the apparatus. The outlets F and K were so arranged that either portion of the main apparatus or both could be exhausted at will. For producing the discharge in AB, the best source of potential was found to be a large static machine, which was not of doubtful or changing polarity as would be the case with an induction coil. The voltage employed was determined by the use of an auxiliary spark gap. The discharges in the tube E and in the comparison spectrum tubes were produced by means of a small induction coil.

IV. CONSTRUCTION AND MANIPULATION.

Much difficulty was at first experienced in the construction of a thin, and yet gas-tight diaphragm at U. To begin with, aluminium foil was used. It was found that the best imported foil was about 0.003 mm. in thickness and was not at all free from holes. Indeed it was impossible to find an area of more than 3 or 4 square mm. which did not have a hole in it. The thinnest aluminium foil which could be obtained in New York City was 0.020 mm. thick, and quite useless because of the immense number of holes in it.

But by using the best white Indian mica and carefully splitting it up with a wedge-pointed laparotomy needle, it was possible to obtain sheets of mica of the required dimensions between 0.002 and 0.006 mm. thick, and free from all visible imperfections. These sheets of mica were sealed in place with De Khotinsky cement which was sprinkled carefully over the sealing metal surfaces in the form of powder and then melted into a smooth film, thus insuring gas-tight contact. Both the front and rear surfaces, *U* and *V*, were thus treated and firmly screwed together while hot with the diaphragm between them.

Careful tests repeated many times established the fact that when the pressure on one side of the diaphragm was 0.0001 mm., the pressure on the other side might be 2,000 times as much without any perceptible leakage occurring in intervals of an hour or more.

In operation, the tube *AB* was exhausted to a pressure of a few hundredths of a mm. or less and the portion *CKD* to below 0.0001 mm. The discharge in *AB* from the static machine was then started. In order to eliminate so far as possible the foreign gases occluded in the electrodes or glass of the main tube, the discharge was run in one direction for some hours and then in the reversed direction for some hours with the pumps working all the time. The capillary discharge tube *E* received similar treatment. At the same time the air-tightness of the diaphragm was tested.

A pink fluorescence at certain spots of the tube, accompanied by considerable heating, was at times observed. This phenomenon was first described by J. E. Lilienfeld[1] and explained by Gehrcke and Reichenheim,[2] who showed that it was due to cathode rays coming from secondary cathodes on the walls of the tube.

The potential in the main tube was adjusted by altering the pressure therein. On running a discharge through *E*, the spectrum of the gas which had accumulated in *CKD* could be examined. In order to get a bright spectrum with only small quantities of gas present, all the gas in *D* was compressed to several thousand times its original pressure by running mercury from *H* through *I* and *D* to *J* and then shutting the cock *J*. A brilliant discharge was then obtained in *E*.

For a time the mercury lines showed uniformly in the apparatus, and it was thought necessary to freeze out the mercury with liquid air. *G* was added for this purpose. It proved, however, that the improved construction which was then adopted with a stop-cock at the top of the compression reservoir prevented the mercury from volatilizing, because the cock could be kept shut during the discharge. The capillary electrodes were never permitted to come into contact with the liquid mercury which clings to them tenaciously.

A preliminary test then showed that after putting fresh air into the apparatus, running the main tube for 15 minutes with the capillary portion isolated, and compressing the gas from the space D into E, only a weak air spectrum could be detected in the capillary tube E when a discharge was passed through it.

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[1] Deutsch. Phys. Gesell. Verh., *8*, 23, p. 631, 1906.

[2] Deutsch. Phys. Gesell. Verh., *9*, 21, p. 593, 1907.

That the spectrum of the gas which reaches CKD may be expected to be visible is shown by the following roughly approximate calculation. Let it be assumed that the current through the main discharge tube is I, and that the fraction $1/R$ of the current carrying positive ions of the kind finally identified in the capillary compression chamber pass through the diaphragm. These may not be charged atoms of the gas with which the main tube has been filled, but may be previously occluded hydrogen atoms which have been shot through the diaphragm, and in this case the fraction $1/R$ may become quite small. On the other hand, if the charged atoms of the gas with which the tube is filled can pass through the diaphragm, $1/R$ will be much larger. Assume also that a spectrum can be observed in the capillary tube when the pressure is $1/P$ atmospheres.

Let that portion of the gas in CKD which is trapped in the compression chamber be $1/n$ of the whole, and let the volume of that chamber be V c.c. When the gas contained therein is compressed into the capillary, let the compression ratio be $c : 1$. The charge on an ion is e.

The current through the diaphragm is $I/2R$. Thus $I/2Re$ ions pass through the diaphragm per second. The number of these which reach each c.c. of the compression bulb after t seconds is $I\ t/2\ RenV$. When these are compressed into the capillary, there will be present in each c.c. $Itc/2\ RenV$ ions which have become neutralized by the addition of negative electrons, that is, molecules.

If under normal conditions of temperature, there are N molecules per c.c. in a gas at atmospheric pressure, the observation of a visible spectrum requires that

$$\frac{Itc}{2\ RenV} = \frac{N}{P}, \qquad \text{and therefore}$$

$$t = \frac{2\ RenVN}{PIc}.$$

The following are estimated and approximate values of the quantities present in the formula: $N = 2.7(10)^{19}$, $R = (10)^6$ when the tube is filled with gases other than those finally detected back of the diaphragm, or $R = (10)^3$ when the tube is filled with a gas which is later found back of the diaphragm, $e = 4.9\ (10)^{-10}$ E. S. U., $I = 1.5\ (10)^6$ E. S. U., $n = 3$, $P = 2.5\ (10)^5$, $c = 5\ (10)^3$, $V = 100$.

Depending on the value of R which applies, $t = 4{,}000$ or 4 seconds. The values observed were one-half and ten times these calculated quantities respectively, so that this extremely rough approximation is consistent with the results obtained.

V. Experiments in Various Gases.

The actual course of the experiments was as follows. After taking the precautions outlined above to ensure the absence of any further large evolution of gas from the electrodes or of leakage through the diaphragm, the tube was run steadily at nearly constant voltage. The gas in the capillary tube was then spectroscopically examined after compression, and showed only a weak air spectrum due to unremoved air.

With the main tube containing air, and a voltage across it of 35,000, after 60 minutes running only the air spectrum of less than its original brightness showed in the capillary. After 90 minutes, however, a weak hydrogen spectrum showed which steadily became more brilliant till a very clear and complete hydrogen spectrum showed after 150 minutes. This spectrum was compared line for line with various standard spectrum tubes which could be compared with each other, and the identification of the hydrogen spectrum was complete. On reducing the voltage across the main tube to 25,000 by increasing the pressure, 120 minutes were required to show a weak hydrogen spectrum; and when the voltage was reduced to 8,000 with the corresponding rise in pressure, no hydrogen spectrum could be seen even after 300 minutes.

Carbon dioxid, carefully freed from water vapor, was then substituted for air in the apparatus. With a voltage of 28,000 the hydrogen spectrum showed after 30 minutes, and as before the spectrum became stronger with time. When the voltage was reduced to 22,000, 60 minutes were required for a visible spectrum. And with a voltage of 6,000 only an extremely doubtful trace of a hydrogen spectrum was observed after 360 minutes.

When argon was placed in the apparatus, it was hard to get a brilliant discharge through the main tube at the lower pressures, and the fluorescence was comparatively dim. With a voltage of 40,000 after 120 minutes a faint hydrogen spectrum was found, which spectrum became more brilliant and complete after continued running. When the voltage was 34,000, 180 minutes were needed for the development of a faint hydrogen spectrum. A prolonged test, wherein the tube was run at 8,000 volts for over 400 minutes showed no hydrogen spectrum.

To remove all traces of argon, which, as several investigators found, clings tenaciously to the electrodes, the tube was washed out repeatedly with air, the electrodes being approximately freed from occluded gas by constant powerful discharges through the main tube and the capillary portion.

Helium was then introduced. As before, the hydrogen spectrum was visible after 60 minutes running when the discharge voltage was 25,000 and 120 minutes sufficed when the voltage was 20,000. At 8,000 volts it was believed that the hydrogen lines could be very faintly seen after 300 minutes running, but since these lines remained extremely dim even after continued running, this observation was regarded as of little weight.

There was one important respect in which helium differed from the other gases examined, namely, that while the hydrogen spectrum developed in time in the capillary, the helium spectrum did the same. Attention was first directed to this point by the brightness of the helium lines which appeared in the discharge capillary with the hydrogen lines after continued running. It was found that both hydrogen and helium passed through the diaphragm.

From the nature of the first experiments, since the apparatus was in any case filled with helium, it was doubted whether this observation was due to actual passage of the helium through the diaphragm. To test this point further, the main tube was filled with helium at appropriate pressure, and the portion *CKD* was washed out with air and then pumped to a low pressure. Thus there was no helium spectrum obtained from the capillary discharge tube at the beginning of the experiment. Experiment then showed that helium did accumulate in the capillary at what was estimated as more than fifty times the rate of accumulation of hydrogen. The helium passed through the diaphragm at 20,000 volts and probably also at considerably lower voltages.

This result is quite explicable, for J. J. Thomson found that in helium, the canal rays were made up of hydrogen atoms, hydrogen molecules, and helium atoms. The large preponderance of the helium atoms in the discharge tube and their consequent carriage of the greater part of the current account for the rapid rate at which the helium passed through the diaphragm.

The main tube was then filled with hydrogen, and the capillary portion with air, the tube and electrodes being first thoroughly cleaned as in the case of argon. Experiment showed that even with so low a voltage as 10,000 and 300 seconds for the discharge period, the hydrogen spectrum was visible in the capillary. At higher voltages, the time was more than proportionally diminished. The mean of a number of observations on the various gases is shown graphically in Fig. 2.

A number of tests were made to determine the effect of a mixture of hydrogen and air in the main tube. Mixtures of hydrogen and air in known proportions were therefore placed in the main tube, and air alone in the capillary portion. The influence of the hydrogen present in the main tube on the time of appearance of the hydrogen spectrum was very marked. Whereas pure air in the main tube yielded at 25,000 volts a hydrogen spectrum in the capillary in 7,200 seconds, 0.1 per cent. of hydrogen mixed with the air reduced this time to 900 seconds, 1.0 per cent. of hydrogen to 200 seconds, 10 per cent. of hydrogen to 100 seconds, and 50 per cent. or more of hydrogen reduced the time of appearance of the hydrogen spectrum to practically the same value as for pure hydrogen, namely, 60 seconds. Similarly, at the lower voltage of 10,000 pure air showed no hydrogen spectrum in the capillary after 18,000 seconds, and 0.1 per cent. of hydrogen nothing after 9,000 seconds, yet 1.0 per cent. of hydrogen showed the hydrogen spectrum after 600 seconds, and greater percentages of hydrogen acted practically the same as pure hydrogen.

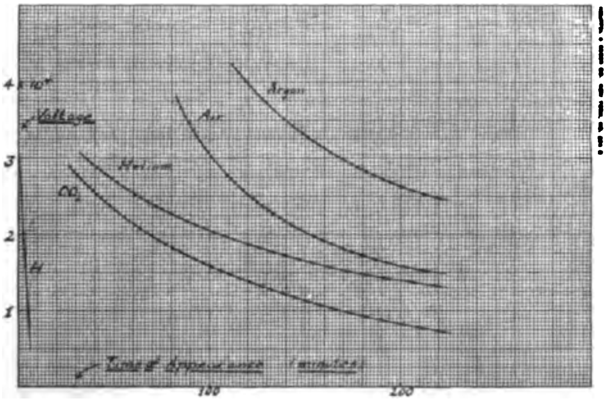

Fig. 2.

A graphical representation of the effect on the time of appearance of the hydrogen spectrum caused by admixture of various proportions of hydrogen with the air in the main tube is given in Fig. 3.

Finally a test, wherein air containing 1 per cent. of helium was used in the main tube, gave a result quite similar to that described above for hydrogen. That is, the helium spectrum appeared in 360 seconds as against 90 seconds for the case where the discharge tube was filled with pure helium. However, air to which about 3 per cent. of argon was added showed no trace of argon in the capillary tube even after 12,000 seconds, so that clearly the argon atoms do not pass through the diaphragm as do the hydrogen and helium atoms.

To ascertain whether the retrograde and cathode rays would show similar effects, the polarity of the electrodes on the main tube was reversed in several tests. No hydrogen or helium spectrum was detected at any time under these circumstances. This experiment afforded an additional proof that the hydrogen found in the capillary was actually due to the canal rays.

In the above experiments attention was fixed on the red hydrogen line (*C*) because of the ease with which it can be identified. Its position was found from a standard comparison spectrum tube at the time of observation and also from the previously calibrated scale of the spectrometer. Since the time of appearance of this line depended on visual acuity and sensitiveness, that is, on physiological factors, not any great accuracy can be attached to the numerical estimates of the time of first appearance of the spectrum. Experience and the maintenance of nearly constant conditions reduced the errors, it is believed, to a small value.

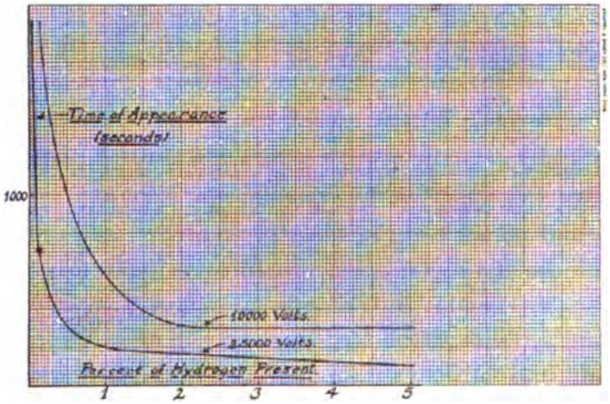

Fig. 3.

In every case (except for the lowest voltage used with each gas) the discharge in the main tube was continued until the entire spectrum was so clear and unmistakable as to check perfectly with the comparison spectrum even with casual visitors observing. Traces of lines not checking with the comparison spectra were carefully searched for, but no unidentified lines were found.

VI. Electric and Magnetic Deflections.

An attempt was made to further identify the moving particles which passed through the diaphragm by obtaining their electric and magnetic spectra by the method of Thomson and Wien. In this case, all the holes but one in the front plate *U* were blocked, and a fine bore tube was placed back of this hole. The apparatus was so arranged that the beam of canal rays was to pass through a magnetic field of known strength and between aluminium plates maintained at a known difference of potential. They were then to strike a fine grained screen of willemite, where their point of impact was to be marked by a bright spot.

The following calculation, however, made it questionable whether the particles which passed through the diaphragm would have a high enough velocity to produce detectable fluorescent effects. Consider the hydrogen atoms which pass through the diaphragm. Imagine that these ions owe their entire velocity to the potential gradient actually existing in the main tube through which they have passed. Let m be the mass of an ion, v its velocity, V the difference of potential of the main tube electrodes, and e the charge of the ion. Then

$$\tfrac{1}{2}mv^2 = Ve.$$

But for hydrogen V is approximately 30,000 volts, $e/m = 10^4$ E.M.U. $= 3\,(10)^{14}$ E.S.U., and therefore $v = 2.5\,(10)^8$ cm. per second. Similarly the value for the helium atom is $v = 1.7\,(10)^8$ cm. per second. It must be remembered that these are the velocities of the ions at the instant that they strike the diaphragm; their velocity after passing through the diaphragm is undoubtedly much lower. The α particle, which is a charged helium atom, has not been actually observed to produce ionization (as detected through fluorescence) at lower velocities than $6\,(10)^8$ cm. per second, 27 per cent. of the maximum velocity. But it is quite possible and even highly probable that it can penetrate matter at lower velocities. So that, though the atoms of hydrogen and helium pass through the diaphragm, their passage was not regarded as proof that they might be expected to show a bright spot on the willemite screen.

Another possible factor in the production of fluorescence must also be considered, namely that the fluorescence may be dependent on the charge carried by the ion as well as on its velocity. Thus, though the velocity of the atoms which pass through the diaphragm might be above the value determined by J. Stark[1] to be necessary for a positive ion to produce fluorescence, yet the neutralization of the charge of the ion on its passage through the diaphragm might prevent the subsequent appearance of fluorescence.

A considerable number of experiments with air, hydrogen, and helium showed that no bright spot could be obtained. The pressure and voltage in the tube were varied through the widest attainable limits, and powerful oscillatory discharges were sent through the main tube as well as the unidirectional discharges. The space back of the diaphragm was pumped to the lowest vacua so that the passage of the rays would not be impeded, the eye of the observer was specially rested to secure maximum visual sensitiveness, and the hole through which the ions passed had its dimensions altered several times. Finally the original diaphragm was replaced by one of less than 0.001 mm. in thickness. In no case could any definite bright spot be detected.

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[1] Ann. d. Physik, *21*, 3, p. 429, 1906.

VII. Conclusions.

1. Canal rays made up of ions of hydrogen or helium can be given sufficient velocity to cause them to pass through thin material partition.
2. When the discharge tube is filled with air, carbon dioxid, or argon the only rays that pass through a thin partition are hydrogen.
3. When helium is used, both helium and hydrogen atoms pass through the partition, the helium in great abundance.
4. When hydrogen is used, only hydrogen atoms pass through the partition, and these in large quantities.
5. The atoms which pass through such a partition are not capable of causing fluorescence on screens.

In conclusion, I desire to express my thanks for the assistance rendered by Professor Bergen Davis, at whose suggestion this research was undertaken.

Phœnix Physical Laboratories,
Columbia University,
August, 1911.

THE MAGNETO-OPTCIAL PARAMETERS OF IRON AND NICKEL.

By Chester Snow.

DURING the last decade a large amount of experimental work has been done upon the Faraday and Kerr effects of the magnetic metals, largely in the visible spectrum, where the range is so limited that the observations give us very little clew as to the trend and cause of the phenomena. Most of these researches have been carried on without reference to any theory (which indeed has been lacking). The theory of Voigt[1] is perhaps the most complete recent attempt towards a unified view of magneto-optical phenomena. It is a first approximation on the basis of the modern electron theory, and as such it makes all types of Kerr and Faraday effects depend uniquely upon the value of a certain complex parameter of the metal, Q.

This constant, which arises from the vibrations of free and bound electrons, is proportional to the inner field or magnetization and is so small that its square is neglected. It is defined as[1]

$$Q = -\frac{4\pi}{\mathrm{n}^2}\sum\frac{Ne^3\nu H}{c(k+i\nu h-m\nu^2)^2},$$

where n is the complex index of refraction in the unmagnetized state, and the summation extends to the different types of electrons present. Its dispersion may thus be determined theoretically when the ordinary dispersion of these metals shall have been worked out and their resonance periods located. Without waiting for this development one can compute the dispersion of Q, as in the present paper, from one class of facts and use it to compare the theory with a different class of observations.

Even though we should not wish to attribute to it the exact meaning it has on Voigt's theory, the importance of this parameter can scarcely be overestimated; for not only does it enable us to explain the variation of polar and meridional Kerr effects with the angle of incidence, but, as we shall show, the recent experiments of Ingersoll[2] on equatorial rotations might have been predicted from a knowledge of it. We shall also compute from these experiments in the infra-red spectrum, and from those of

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[1] W. Voigt, Magneto- und Elektrooptik, 1908, p. 293.

[2] L. R. Ingersoll, Phys. Rev., 35, p. 312 (1912).

Foote[1] on polar magnetic rotation and ellipticity in the visible spectrum, the values of this constant for nickel and iron from wave-length .4 μ to 2.1 μ and use it to compare the consequences of the theory with the results of a number of other experimenters on the Kerr and Faraday phenomena of these metals.

I. EQUATORIAL KERR EFFECT.

The peculiar curves given by Ingersoll showing the dependence of the equatorial rotation on the angle of incidence were compared by him with the theoretical predictions of C. H. Wind.[2] The agreement in the case of iron was remarkable, although for cobalt and nickel it seemed to be merely qualitative. We shall see that the agreement in the case of Voigt's theory is all that could be desired for all three of these metals.

Let a plane wave fall upon a tangentially magnetized mirror at an angle of incidence ϕ, the plane of incidence being perpendicular to the magnetization. Let the electric vectors in and normal to the plane of incidence be the real parts of $E_pe^{i\nu t}$ and $E_se^{i\nu t}$ respectively. Let the corresponding components of the reflected ray be $R_p \equiv Fe^{-if+i\nu t}$ and $R_s \equiv Ge^{-ig+i\nu t}$ respectively. When the incident light is linearly polarized E_p and E_s are real and $E_s/E_p = \tan X$, where X is the azimuth of the electric vector. Voigt in considering this case makes certain approximations which render his final formula inapplicable to large angles of incidence. We shall get the correct expression for all incidences by starting from his equation[3] for the ratio of the reflected amplitudes, which is

$$\frac{R_s}{R_p} \equiv \frac{G}{F}e^{-i(g-f)} = -\frac{E_s}{E}\frac{\cos\phi - \mathrm{n}\alpha'}{\cos\phi + \mathrm{n}\alpha'}\cdot\frac{\alpha' + \mathrm{n}\cos\phi + i\dfrac{Q\sin\phi}{\mathrm{n}}}{\alpha' - \mathrm{n}\cos\phi + i\dfrac{Q\sin\phi}{\mathrm{n}}}, \qquad (1)$$

where $\mathrm{n} = n(1 - ik) = n\sqrt{1 + k^2}e^{-i2\Theta} = \sin\Phi\tan\Phi e^{-i2\Theta}$ and $k = \tan 2\Theta$, $\sin\Phi\tan\Phi = n\sqrt{1 + k^2}$, n and k being the ordinary refractive index and absorption index, and

$$\alpha' = \sqrt{1 - \frac{\sin^2\phi}{\mathrm{n}^2}}.$$

Treating Q as a first order small quantity this may be written

$$\frac{R_s}{R_p} \equiv \frac{G}{F}e^{-i(g-f)} = -\frac{E_s}{E_p}\cdot\frac{\cos\phi - \mathrm{n}\alpha'}{\cos\phi + \mathrm{n}\alpha'}\cdot\frac{\alpha' + \mathrm{n}\cos\phi}{\alpha' - \mathrm{n}\cos\phi}\cdot\left(1 - \frac{iQ\sin 2\phi}{\alpha'^2 - \mathrm{n}^2\cos^2\phi}\right).$$

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[1] P. D. Foote, PHYS. REV., 34, p. 96 (1912).

[2] C. H. Wind, Arch. Neer., II., 1, p. 119 (1898).

[3] Loc. cit., p. 320.

In Ingersoll's experiment the azimuth of the polarizer is adjusted to a value X_0 such that the magnitudes of the reflected components F and G are equal, as indicated by the bolometer. Their phase difference is immaterial. The magnetic field is then created and the small rotation δX of the polarizer, which is necessary to restore the equality to the reflected components is measured. Using subscripts $_0$ to denote ordinary values (with zero magnetization, *i. e.*, $Q = 0$) and putting $F = G$ in each case we have if $\delta \equiv g - f$

$$e^{-i\delta} \cot X = -\frac{\cos\phi - n\alpha'}{\cos\phi + n\alpha'} \cdot \frac{\alpha' + n\cos\phi}{\alpha' - n\cos\phi}\left(1 - \frac{iQ\sin 2\phi}{\alpha'^2 - n^2\cos^2\phi}\right)$$

and

$$e^{-i\delta_0} \cot X_0 = -\frac{\cos\phi - n\alpha'}{\cos\phi + n\alpha'} \cdot \frac{\alpha' + n\cos\phi}{\alpha' - n\cos\phi}.$$

Dividing the upper by the lower equation we get

$$e^{-i(\delta-\delta_0)}\frac{\tan X_0}{\tan X} = 1 - \frac{iQ\sin 2\phi}{\alpha'^2 - n^2\cos^2\phi} = 1 - \frac{iQ\sin 2\phi}{1 - \dfrac{\sin^2\phi}{n^2} - n^2\cos^2\phi}.$$

For brevity let us put $b = n^2(1 + k^2)$ and $Q = |Q| \cdot e^{-iq}$. Then

$$e^{-i(\delta-\delta_0)}\frac{\tan X_0}{\tan X} = 1 + \frac{|Q|\sin 2\phi e^{-i(q+\pi/2)}}{1 - \dfrac{\sin^2\phi e^{i4\Theta}}{b} - b\cos^2\phi e^{-i4\Theta}}$$

$$= 1 + \frac{|Q|\sin 2\phi\, e^{-i(q+\pi/2+\theta)}}{\sqrt{\left[1 - \dfrac{\cos 4\Theta(b^2\cos^2\phi + 1)}{b}\right]^2 + \sin^2 4\Theta\left[\dfrac{b^2\cos^2\phi - 1}{b}\right]^2}}$$

where

$$\tan\theta = -\tan 4\Theta\frac{b^2\cos^2\phi - 1}{b^2\cos^2\phi + 1 - b\sec 4\Theta}, \qquad (2)$$

b^2 being written for $b^2 + 1$ since in nearly all cases considered $b^2 > 100$. If we write for brevity

$$y = \sqrt{b^2\cos^4\phi - 2[(b - 2\cos 4\Theta)\cos 4\Theta + 1]\cos^2\phi + 1 - \frac{2\cos 4\Theta}{b}}, \qquad (3)$$

then

$$\frac{\tan X_0}{\tan X} = \left\{1 - \frac{|Q|\sin 2\phi\sin(\theta + q)}{y}\right\} \cdot e^{-i\left[\delta_0 - \delta + \frac{|Q|\sin 2\phi\cos(\theta+q)}{y}\right]},$$

from which, equating argument and modulus, we get

$$\delta - \delta_0 = \frac{|Q| \sin 2\phi \sin (\theta + q)}{y}, \tag{4}$$

$$\tan X = \tan X_0 \left\{ 1 + \frac{|Q| \sin 2\phi \sin (\theta + q)}{y} \right\}, \tag{5}$$

or since

$$X = X_0 + \delta X$$

$$2\delta X = \frac{|Q| \sin 2\phi \sin 2X_0 \sin (\theta + q)}{y}, \tag{6}$$

X_0 is given by[1]

$$\cos 2X_0 = \frac{2n \sin \phi \tan \phi}{\sin^2 \phi \tan^2 \phi + b}. \tag{7}$$

The magnetic phase change is given by (5), the double magnetic rotation of Ingersoll's experiments by (6). The latter is plotted in Fig. 1 as a function of the angle of incidence for iron, nickel, and cobalt

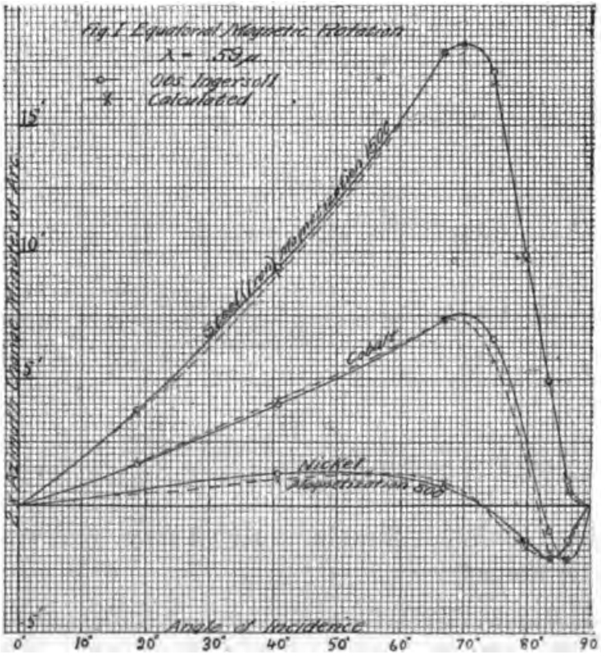

Fig. 1.

at the wave-length of sodium light, and is in striking agreement with the observations for all three metals. The constants $|Q|$ and q were chosen so as to fit two points on a curve.

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[1] P. Drude, Lehrbuch der Optik, p. 33.

II. Computation of Parameters.

As Ingersoll gives a curve for each of several wave-lengths in the visible and infra-red spectrum, the values of $|Q|$ and q have been computed for these wave-lengths from his curves by means of equations (2), (3), and (6). The constants for the remainder of the visible spectrum have been computed from Foote's measurements of the rotation R and ellipticity E of light reflected normally from massive mirrors magnetized perpendicularly to their surfaces. The formulæ are[1]

$$R = -\frac{|Q| \sin (2\Theta - q)}{\sin \Phi \tan \Phi}, \tag{8}$$

$$E = -\frac{|Q| \cos (2\Theta - q)}{\sin \Phi \tan \Phi}. \tag{9}$$

Rotations and ellipticities are considered positive when they correspond to directions parallel to the magnetizing current.

The value of q is characteristic of the metal and independent of the magnetization while $|Q|$ on the other hand is proportional to it. The values of q from the two sets of data, where they overlap in the visible spectrum, are in good agreement. $|Q|$ was found to be 15 per cent. higher in the case of iron (steel) and 20 per cent. higher in the case of nickel, when computed from Foote's measurements and this was taken as a measure of the relative magnetizations in the two cases. The latter values of $|Q|$ were all accordingly reduced by a constant factor to bring equality at .59 μ. The computations require a knowledge of n and k at each wave-length, and these were taken from a paper by Ingersoll.[2] The computed values of these parameters for nickel and iron are given in the following table.

The tabulated values are plotted in Fig. 2. As we should expect there is more uniformity in the values for q than for $[Q|$ since the former is independent of magnetization. The assumption that Q is real, as in the earlier theories, is seen to be not even approximately correct, except in the case of iron near the wave-length of sodium light.

The agreement of the two sets of data in the yellow and red end of the visible spectrum where they overlap, means that from one set of observations the other could have been predicted. As a striking example, the reversal of sign of the ellipticity of the normally reflected light from nickel, which was found by Foote and also by Dzwulski,[3] to take place with polar magnetization between the wave-lengths .57 μ and .6 μ,

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[1] Voigt, loc. cit., p. 316.

[2] L. R. Ingersoll, Astrophys. Jour., 32, p. 265 (1910).

[3] W. Dzwulski, Phys. Zeit., 13, p. 642 (1912).

TABLE I.

Wave-length.	Iron (Steel).		Nickel.		Computed from Observations of
	q	$\|Q\|$ Mag. 1500.	q	$\|Q\|$ Mag. 500.	
.42μ	+15.0°	.019	− 9.0°	.006	Foote (polar effects)
.50	+10.0°	.025	− 20.0°	.007	Foote (polar effects)
.59	+ 2.4°	.032	− 27.5°	.0081	Foote (polar effects)
.59	+ 2.5°	.032	− 28.0°	.0081	Ingersoll (equatorial effects)
.65	− 4.5°		− 33.0°		Foote (polar effects)
.73	−15.0°	.041			Ingersoll (equatorial effects)
.74			− 52.7°	.0120	Ingersoll (equatorial effects)
.91	−27.0°	.056			Ingersoll (equatorial effects)
1.21	−40.7°	.055			Ingersoll (equatorial effects)
1.24			−109.0°	.0167	Ingersoll (equatorial effects)
1.65	−56.5°	.061			Ingersoll (equatorial effects)
2.10	−72.0°	.060			Ingersoll (equatorial effects)
2.12			−175.0°	.0320	Ingersoll (equatorial effects)

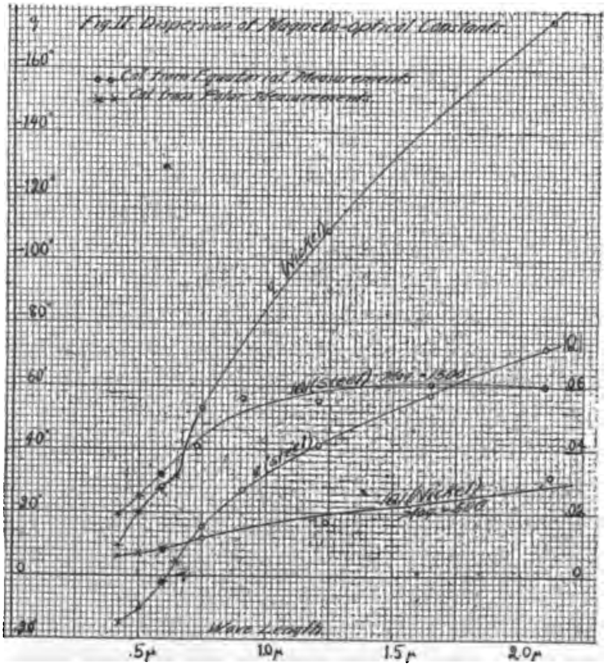

Fig. 2.

should be given by the vanishing of the factor cos $(2\Theta - q)$ of equation (9). Since 2Θ has a practically constant value, 63.3° in this part of the spectrum, the reversal in sign should occur when $63.3° - q = \pi/2$ or $q = -26.7°$. Reference to the table (Ingersoll's data) shows $q = -28°$ at $\lambda = .59\ \mu$ and it is rapidly changing with wave-length. The predicted value of the wave-length of reversal falls between the observed values for two different specimens.

III. Comparison of the Theory with Experiments on Faraday and Polar Kerr Effects.

Voigt does not work out the general expression for the rotation R' and the ellipticity E' of the light transmitted through a thickness e in the direction of the lines of force. The index of refraction of the positive and negative circularly polarized waves in this case is given by[1]

$$\mathrm{n}_{\pm}^2 = n^2(1 \mp Q)$$

or since

$$\mathrm{n} = n(1 - ik) = n\sqrt{1 + k^2}e^{-i2\Theta}$$

$$n_{\pm}^2(1 + k_{\pm}^2)e^{-i4\Theta_{\pm}} = n^2(1 + k^2)\{1 \mp |Q| \cos q \pm i\,|Q| \sin q\}e^{-i4\Theta}$$

or

$$n_{\pm}^2(1 + k_{\pm}^2) = n^2(1 + k^2)(1 \mp |Q| \cos q)e^{-i(4\Theta - 4\Theta_{\pm} \mp |Q| \sin q)}$$

from which, equating modulus and argument we get

$$n_{\pm}^2(1 + k_{\pm}^2) = n^2(1 + k^2)(1 \mp |Q| \cos q),$$

$$2\Theta_{\pm} = 2\Theta \mp \frac{|Q| \sin q}{2}.$$

But

$$k_{\pm} = \tan 2\Theta_{\pm} = \frac{\tan 2\Theta \mp \dfrac{|Q| \sin q}{2}}{1 \pm \dfrac{|Q| \sin q}{2} \tan 2\Theta} = k \mp (1 + k^2)\frac{|Q| \sin q}{2}.$$

From this we find

$$n_{-} - n_{+} = |Q|\, n\sqrt{1 + k^2}\left(\frac{1}{\sqrt{1 + k^2}} \cos q - \frac{k}{\sqrt{1 + k^2}} \sin q\right)$$

$$= |Q| \sin \Phi \tan \Phi \cos (2\Theta + q)$$

and

$$n_{-}k_{-} - n_{+}k_{+} = |Q| \sin \Phi \tan \Phi \sin (2\Theta + q).$$

If a plane polarized wave is incident normally upon the medium, then after travelling in the direction of the lines of force a thickness l centimeters of the metal it will emerge as a slightly elliptically polarized wave in which the major axis of the ellipse makes an angle R' with the incident vibration, where

$$R' = \frac{\pi l}{\lambda}(n_{-} - n_{+}) = \frac{\pi l |Q|}{\lambda} \sin \Phi \tan \Phi \cos (2\Theta + q). \qquad (10)$$

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[1] Loc. cit., p. 297.

The ratio of the axes of the ellipse (or the ellipticity) is

$$E' = \frac{\pi l}{\lambda}(n_- k_- - n_+ k_+) = \frac{\pi l \mid Q \mid}{\lambda} \sin \Phi \tan \Phi \sin (2\Theta + q), \tag{11}$$

where as before the positive direction of rotation is that of the magnetizing current.

The proportionality of R, R', E, and E' to the magnetization, that is, to $\mid Q \mid$, as indicated by the equations (8), (10), (9), and (11) respectively, has been shown experimentally by DuBois,[1] Kundt,[2] Foote,[3] and Skinner and Tool,[4] respectively. The values of these four quantities for iron (steel) and nickel calculated for the wave-length of sodium light are shown in Tables II. and III. together with observed values for comparison.

TABLE II.

Iron (Steel).

$\lambda = .59 \mu$.

Polar Kerr Rot. R.	Polar Kerr Ellipt. E.	Faraday Rot. per cm. R'.	Faraday Ellipt. per cm. $E' \times 10^3$.	Magnetization.	
−20.5′	.0044	219,000°	6	1,500	Computed from equatorial measurements
−23′				1,700	Observed by Du Bois
−23′ to 24′	−.0050			1,520	Observed by Foote
		200,000°		saturated	Observed by Lobach[5] (electrolytic iron)
		275,000°	4	saturated	Observed by Skinner and Tool (electrolytic iron)

TABLE III.

Nickel.

$\lambda = .59 \mu$.

Polar Kerr Rot. R.	Polar Kerr Ellipt. E.	Faraday Rot per cm. R'.	Faraday Ellipt. per cm. E'.	Magnetization.	
−7.5′	0	75,000°	1	500	Computed from equatorial measurements
−9.0′	0			600	Observed by Foote
		78,000°		saturated	Observed by Lobach
			0		Observed by Harris

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[1] H. DuBois, Wied. Ann., 39, p. 25 (1890).

[2] A. Kundt, Wied. Ann., p. 199 (1886).

[3] P. D. Foote, PHYS. REV., 34, p. 96 (1912).

[4] C. A. Skinner and A. Q. Tool, Phil. Mag., 16, p. 833 (1908).

[5] W. Lobach, Wied. Ann., 39, p. 347 (1890).

The equation (11) together with the tabulated values of the constants shows that the ratio of the ellipticity to be expected when light is transmitted through nickel to that produced by an iron film of equal density is $\frac{|Q|_{\text{Ni}}\sin 35^\circ}{|Q|_{\text{Fe}}\sin 58^\circ}$, or 1/6, for sodium light. Since the latter is so small as to be observed with difficulty this probably explains why Harris[1] failed to detect the magnetic ellipticity produced by nickel films in the transmitted light.

The agreement between observation and theory is better for the reflection phenomena than for those of transmission, probably on account of the difficulty in measuring the thickness of the film.

To test the theory for all wave-lengths from .4 μ to 2.1 μ the curves of Fig. 3 for R, the polar Kerr rotation, have been plotted. The computed

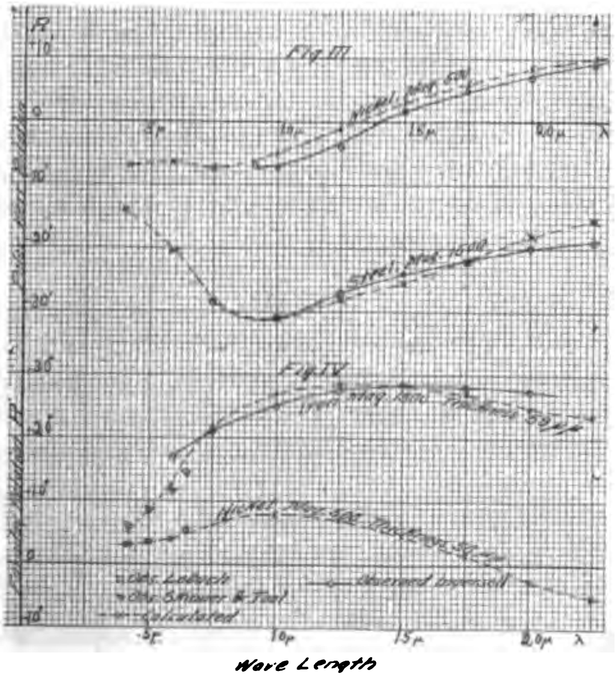

Fig. 3.

values (with the use of equation (8)) are for magnetizations of 1,500, and 500, of the iron and nickel, respectively, for which the above tables of $|Q|$ were computed. They compare favorably with the results obtained by Ingersoll[2] in 1906, which have been doubled to reduce them to the same magnetization. The reversal of the rotation produced by nickel in the neighborhood of wave-length 1.4 μ is seen to be in agreement with the theoretical curve which crosses the axis at wave-length 1.3 μ, the discrepancy being no larger than that between different specimens. This explains a point which has been a matter of some interest.[1]

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[1] W. D. Harris, Phys. Rev., 24, p. 337 (1907).

[2] L. R. Ingersoll, Phil. Mag., 11, p. 41 (1906).

The dispersion of the Faraday rotation has also been computed for the same spectral range and plotted in Fig. 4. The infra-red observations[2] are for an unoxidized iron cathode film 58 $\mu\mu$ thick, and the whole of the iron curve has been plotted for a film of this thickness and a magnetization of 1,500. The observed values have been multiplied by 2.5 which we must assume as the ratio of the magnetizations. This is not surprising on account of the great demagnetizing factor of thin films, and the comparatively low field used in these experiments—in this case 5,700 C.G.S. units. In the visible spectrum the observations of Skinner and Tool are also plotted after being reduced to the theoretical curve for wave-length .5 μ. The theoretical curve for nickel is also drawn: the only available experimental data for comparison are in the visible spectrum where the measurements of Lobach are reduced to the same scale at .5 μ and plotted. The Faraday rotation of nickel should change sign at wave-length 1.85 μ and the ellipticity, though extremely small, should reverse near wave-length .82 μ.

SUMMARY.

1. An expression for the equatorial magnetic rotation has been obtained as a consequence of Voigt's theory, which is in good accord with the recent experiments of Ingersoll. The magneto-optical constants of iron and nickel have been computed from these experiments and from those of Foote.

2. Formulæ for the magnetic rotation and ellipticity for the transmitted light have been obtained and the amounts of the Kerr and Faraday rotation and ellipticity computed for yellow light. These are in close agreement with accepted values.

3. The relative dispersion of these two rotations has been computed for a spectral range from .4 μ to 2.1 μ and is in fair agreement with all the experimental results which have thus far been obtained for nickel and iron.

PHYSICAL LABORATORY,
UNIVERSITY OF WISCONSIN,
May, 1913.

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[1] Cf. St. Loria and Zakrzewski, Acad. Sci. Cracovie Bull., 6a, p. 278 (1910).

[2] L. R. Ingersoll, Phil. Mag., 18, p. 74 (1909).

ON THE BEADED CHARACTER OF THE CATHODE RAY LINE AS REVEALED BY INSTANTANEOUS PHOTOGRAPHS TAKEN AT SHORT RANGE.

By Chas. T. Knipp.

THE magnetic spectrum, so called, of cathode rays has been investigated by Birkeland, Strutt, and Thomson,[1] and is generally conceded to be due to the want of uniformity necessarily associated with the use of an induction coil. It was early shown that similar effects may be obtained by using an electrostatic instead of a magnetic field.

Recently, while photographing at short range the carriers, atomic in size, of both positive and negative electricity that accompany the cathode beam, I was impressed with the beaded character of the cathode ray line. The distinctness and regularity of the beads suggested that their origin might possibly be other than a want of uniformity that accompanies the induction coil or static machine discharge, or other than the presence of secondary rays.

Apparatus and Manipulation.

The apparatus employed was that described in a recent number of the Physical Review.[2] The modifications necessary were slight. The Wehnelt cathode was removed and in its stead an ordinary aluminum cathode was suitably mounted. The beam of cathode rays emergent from the canal passed between the nearly coterminous magnetic poles and electrostatic field plates and fell upon the photographic plate beyond. This range was about 2 centimeters. Seed's lantern slide plates were used. Mounting and exposing a plate to the action of the rays was briefly as follows: The circular plate, fastened to the movable brass disc[3] at three points by means of half and half wax, was placed in the cylindrical plateholder, which in turn slipped into position in the apparatus. After connecting the winch for turning the plate the glass containing vessel was sealed and the pump started. When the desired degree of exhaustion was reached, either with or without the aid of charcoal and liquid air, the electrostatic field was turned on and the discharge started. To get instantaneous photographs it was only necessary to rotate the plate while the discharge was passing.

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[1] J. J. Thomson, Conduction of Electricity through Gases, 2d ed., p. 633.

[2] C. T. Knipp, Phys. Rev., XXXIV., March, 1912.

[3] See Fig. 1 of article referred to above.

Thus under varying conditions of deflecting fields (either magnetic, electrostatic, or both), aperture, vacuum and source of discharge, together with varying conditions of resistance, self-induction, and capacity in the circuit, photographs of great diversity were possible. The short range that the carriers traveled enabled impressions to be received and recorded on the plate that at greater distances would doubtless be lost because of absorption.

GENERAL CONSIDERATIONS.

The electrostatic displacement of the cathode ray particle as recorded by the photographic plate is given by the equation

$$x = \frac{Ae}{mv^2}, \tag{1}$$

while the magnetic displacement is

$$y = \frac{Be}{mv}, \tag{2}$$

where A and B are constants depending upon the strength of the two fields respectively and upon the geometrical data of the discharge vessel. From these it follows that for a given range of velocities the greatest dispersion is to be had when an electrostatic field is employed. If there are present carriers having a wide range of velocities, falling off gradually from a maximum, then the time exposures when either field is employed should appear on the plate as a straight line shading off gradually in intensity as you recede from the geometrical or undeflected spot. The character of the instantaneous photographs will depend upon whether the discharge is intermittent or not. In the former case, the case of an induction coil discharge, the instantaneous exposures will be similar in shape and shading to the time exposures, only much less intense. If, however, the discharge is continuous, such as may be had from a high potential storage battery, the instantaneous exposures should reveal a continuous uniformly drawn out band similar in shading to the time exposure only much less intense. Uniformity in the direction of rotation of the continuous band may be expected only when the plate is rotated with uniform velocity.

It would seem, then, that under the conditions just stated this arrangement of apparatus should reveal radiations that might have their origin in the discharge and possess energy enough to affect a photographic plate, as for instance (1) the presence of carriers due to ionization or secondary effects, (2) the possible emission of group velocity electrons from the surface of the cathode, or (3) group velocity electrons that may have their rise in the oscillatory character of the electric discharge.

In the first case, that of ionization, it is reasonable to expect that the photographs should show configurations that are fixed for both the time and the instantaneous exposures, but that would not necessarily be the same for a succeeding plate, and in general would not follow a definite law or sequence. In other words, the instantaneous photographs of the cathode ray line, produced by say an induction coil discharge, might show beads due to ionization and secondary effects, but it is not likely that the spacing of these beads along the line would follow any definite sequence though the spacings from instantaneous photograph to instantaneous photograph for a given plate more than likely would be the same.

In the second case if the cathode gave off group velocity electrons the effect on the plate should be marked—both for time and instantaneous exposures. Again, it does not seem clear that any definite spacing of the beads should be expected though the spacing, whatever it might have, would be characteristic of the metal. That the cathode gives off simultaneously group velocity electrons is by no means assured, though a careful study of the photographs lends that view some support.

Finally in the case of group velocity electrons that have their rise, when the discharge is intermittent, to the oscillatory character of the discharge we can foretell quite accurately what the effect on the photographic plate should be for both time and instantaneous exposures. Take the case of the discharge passing between the knobs of a static machine when the leyden jars that accompany the machine are included. The discharge obviously is oscillatory though damped rapidly. Let its general character be represented by Fig. 1, in which the ordinates represent successive values of the quantity of electricity discharged and the abscissas the periodic time T. This period is given by the relation

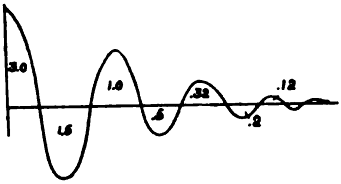

Fig. 1.

$$T = 2\pi \Big/ \sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}},$$

which, as R diminishes, approaches the value

$$T = 2\pi\sqrt{LC}.$$

In words, the curve approaches a simple sine wave with no damping.

If such an electrical pendulum could maintain itself in the case of our discharge vessel, the kinetic energy would remain constant and there would in consequence result but one group of group velocity electrons. This group would have the same velocity as the electrons in the case of a continuous discharge corresponding to the same discharge potential difference. If however R has a considerable value, as is the case that obtains in the ordinary operation of a discharge tube by a static machine or induction coil, the oscillations are damped as shown in Fig. 1. The successive quantities discharged through the tube fall off rapidly, and hence the energy also falls off rapidly. This results, since both e and m remain constant, in a number of groups of electrons (one group corresponding to each crest) having successively smaller and smaller velocities. Take for example the case when the successive ordinates, both positive and negative, are proportional to 3.0, 1.5, 1.0, 0.5, 0.32, 0.2, 0.12 centimeters. If, as was suggested, the velocities of the resulting electrons in the cathode beam are proportional to these ordinates we should get by equation 1, for the electrostatic displacement, distances proportional to 0.11, 1.0, 10, 25, 70. And similarly by equation 2, for the magnetic displacement, distances proportional to 0.33, 1.0, 3.3, 8.3. These displacements drawn to the same scale are set down in Fig. 2. Hence the number of beads appearing on a given photographic plate, other conditions remaining constant, is, roughly, inversely as the damping of the oscillatory discharge which gives rise to them.

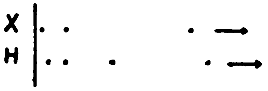

Fig. 2.

The degree of exhaustion would also have an important bearing on the appearance of the beads. For a given set of conditions, such as in the example above, we should expect that the higher the vacuum the greater the velocity of the group electrons and hence the less the displacement. However, if the vacuum is too high the oscillations after the first one may not be able to get through the discharge vessel, and for very high vacua we should expect but the one group. On the other hand if the vacuum is low the velocity of the successive groups will be low and hence the larger the displacements. The latter may be so large for group electrons corresponding to oscillations after the first that these groups may be driven off the plate by the deflecting field. For low vacua the absorption will be considerable and this may be sufficient to prevent the slower moving groups from reaching the plate, or, if they do reach it, as may be the case

TABLE I.

Photographic Plate.	Pressure in Mm. Hg.	Equiv. Spark in Air in Cm.	Aperture.			Electrostatic field in Volts per Cm.	Series Air Gap in Cm.	Source of Discharge.	Time Plate was Developed in Min.	Remarks.
			Kind.	Diam. in Mm.	Length in Mm.					
10	—	—	Diaphragms	.2	9	2,000	1.0	8 inch Leeds coil	2	Commutated electrostatic field.
30	.004	2.5	Tube	.12	18	3,000	1.3	6 inch Kohl coil	7	Electrostatic field only.
33	.004	2.5	Tube	.12	18	3,000	1.0	6 inch Kohl coil	12	Two conditions, see discussion.
46	—	.35	Diaphragms	.2	9	3,000	1.2	8 inch Leeds coil	5	Simple connections.
47	.012	.8	Diaphragms	.2	9	3,000	1.2	8 inch Leeds coil	5	Simple connections.
48	—	1.2	Diaphragms	.2	9	3,000	1.2	8 inch Leeds coil	2	Simple connections.
65	—	.5	Diaphragms	.2	9	1,800	.5	Wehrsen Static Machine	5	Resistance, inductance and capacity.
67	—	—	Diaphragms	.2	9	1,600	1.0?	Wehrsen Static Machine	5	Static machine connected direct.
73	—	2.0	Diaphragms	.2	9	1,800	.3	Wehrsen Static Machine	5	Ditto, also interchanged connections.
76	.012	.8	Diaphragms	.2	9	1,800	1.2	8 inch Leeds coil	5	Interchanged connections.
77	.013	.85	Diaphragms	.2	9	3,000	1.2	8 inch Leeds coil	6	Interchanged connections.
81	—	—	Tube	.12	18	3,000	—	8 inch Leeds coil	8	Interchanged connections.

when the deflecting field is weak, they may not possess enough energy to affect the photographic film.

DISCUSSION OF PHOTOGRAPHS.

As stated at the outset the beaded character of the cathode ray line was observed accidentally while working on retrograde rays. The shutter had failed to work, and in attempting an exposure on a fresh surface the plate was turned forward while the discharge was passing. The plate when developed showed, for the instantaneous exposures, a marked beading. Subsequently the beads were again noticed, especially when one or the other of the deflecting fields was zero. The beads seemed more pronounced when the deflection was due to the electrostatic field and hence most of the exposures (except a few at the beginning), were made with H equal to zero.

Some fifty plates were exposed with especial reference to this beaded effect. A number of these were selected as representative and are reproduced full size in Plates I. and II. The order of exposure is indicated on each photograph. The data relative to these photographs are collected in Table I. It may be well to state that if looking in the direction of the beam of cathode rays, the plates, in exposing, were turned counter clockwise. This makes the order on the reproduced photographs clockwise. The exposures, then, begin at the left and end after a more or less complete clockwise revolution near the beginning.

The photograph reproduced in Fig. 3 was the first to show beads. The deflections were due to both the magnetic and electrostatic fields acting simultaneously. In the first half the direction of the electrostatic field was such as to drive the cathode line away from the center. This field was reversed in the second half. The instantaneous exposures, in general, show three bright spots or beads. No record was kept of the vacuum; however, it was not high.

The reproduction shown in Fig. 4 was one of the first plates exposed in which the sole object was to get the beaded effect. During the interval the diaphragms used in Fig. 3 were replaced by a brass tube about 18 mm. long by .12 mm. internal diameter. This tube gave much sharper definition. The vacuum was high and the minimum discharge potential was equivalent to a 2.5 cm. spark in air. In this and the photographs that follow the electrostatic field only was employed. The photograph shows a series of instantaneous exposures with X (the electrostatic field) equal to zero, a time exposure of 10 or 15 seconds, followed by another series of instantaneous exposures with X = 3,000 volts per centimeter, and finally a time exposure of about one second. Many of the instan-

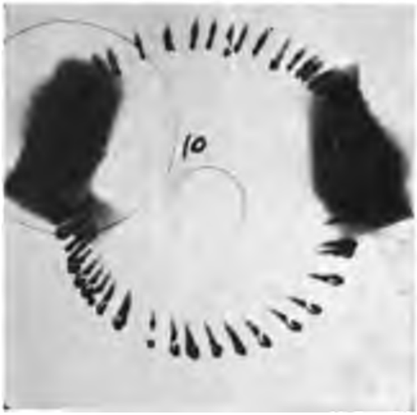

Fig. 3.

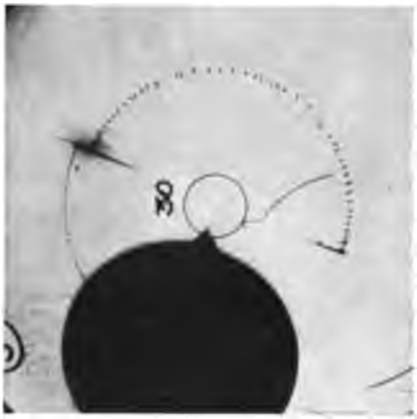

Fig. 4.

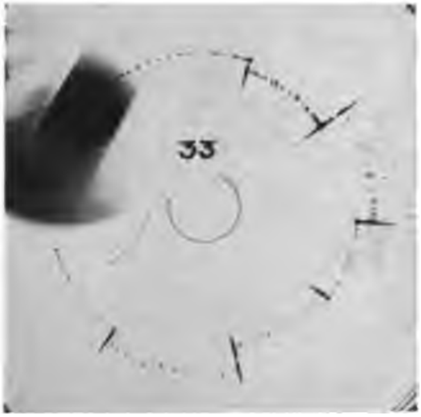

Fig. 5.

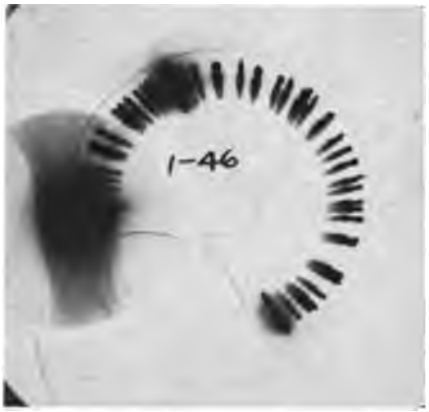

Fig. 7.

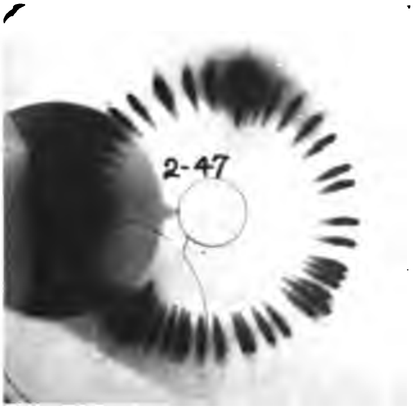

Fig. 8.

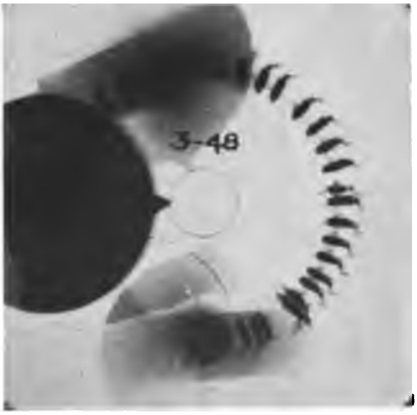

Fig. 9.

PLATE I.

CHAS. T. KNIPP

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July, 1913.

PLATE II.
To face page 44.

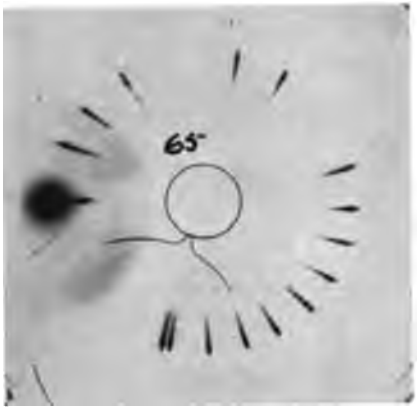


Fig. 10.

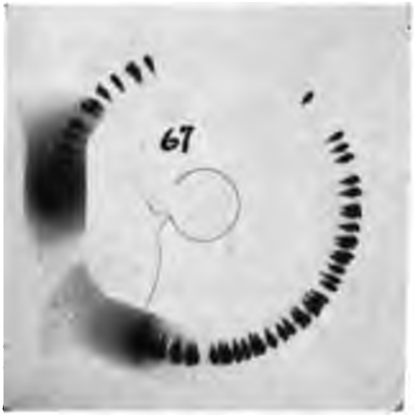


Fig. 12.

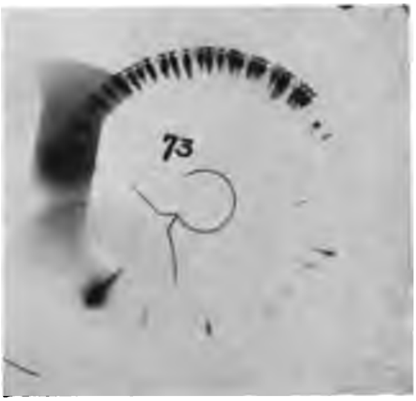


Fig. 13.

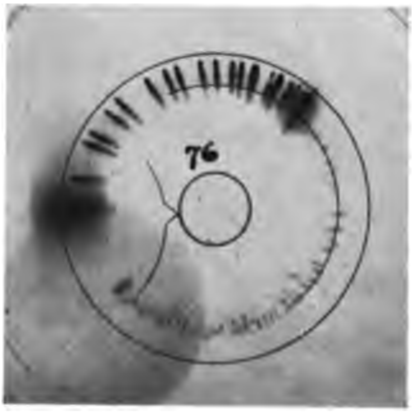


Fig. 14.

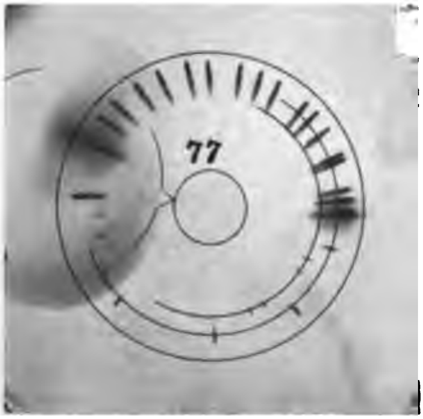


Fig. 15.

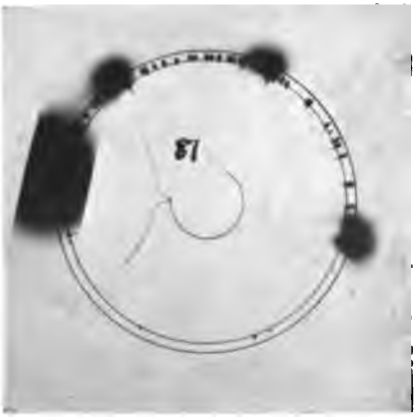
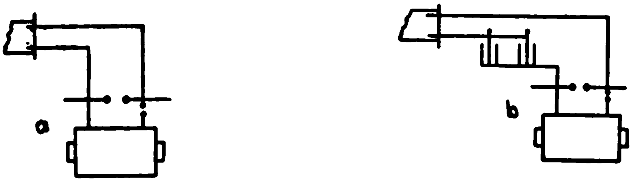


Fig. 16.

PLATE II.

taneous exposures show a second and several a third dot in the direction towards the center of the plate. It is interesting in this connection to note that the first time exposure also shows the retrograde rays, *i. e.*, carriers atomic in size and charged positively and hence deflected, in this photograph, away from the center.

The conditions for Fig. 5 were nearly the same as in Fig. 4, except in the second half of the revolution a capacity of two leyden jars was included as shown in *b*, Fig. 6. The connections for the first half are shown in *a* of the same figure. The undeflected spots are first shown, then the plate was turned through an arc during which the deflecting field *X* was on, after which *X* was reversed for a time and then again reduced to zero. The leyden jars were now included, as shown in Fig. 6, *b*, and the sequence of exposures repeated. Unfortunately the reproduction does not show all of the finer markings of the negative. A number of the exposures on the negative show as many as four beads.



a *b*

Fig. 6.

In the succeeding photographs the tube was replaced by the objective containing the diaphragms. The three photographs, Figs. 7, 8, 9, constitute a series of instantaneous exposures in which all the conditions were kept constant except the vacuum. In these an 8 inch Leeds coil was substituted for the 6 inch Kohl coil. The connections were those of *a*, Fig. 6. The method of exposing each plate was to give the plate a quarter turn, then stop for a few seconds before proceeding on round. The first photograph, Fig. 7, shows the beads in a striking manner. In the second, Fig. 8, the vacuum was some higher and hence the displacement of the first group is less. The exposures on this plate show peculiar markings in the neighborhood of the undeflected point which may be due to ionization or secondary effects. These markings together with others that appear at the side of each instantaneous photograph are distinctly shown in the third photograph of this series, Fig. 9. The effect of an increasing vacuum is to cut off the subsequent groups. Traces of retrograde rays are visible in nearly all of the time exposures on these three plates.

In the next three photographs, Figs. 10, 12, and 13, the induction coil was replaced by a Wehrsen static machine. Smaller values of X were also used. In Fig. 10 the connections were made as sketched in Fig. 11. As is readily seen the discharge takes place at B without preparation whenever a spark passes at A. The volume of the discharge was considerable. Most every instantaneous exposure on the negative shows beads. In the photograph reproduced in Fig. 12 the inductances and leyden jars were removed and connections were made direct. The vacuum was quite high. The peculiar markings shown in Figs. 8 and 9 again appear. These markings also appear very distinctly in the first half of Fig. 13. It would thus seem that they are not dependent upon the source of the discharge.

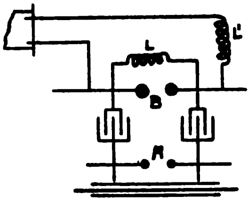


Fig. 11.

To get still further evidence on the possible cause of the beads that so persistently appear on the cathode ray line I followed a suggestion made by Mr. O. H. Smith, graduate student in physics, and who assisted me in making a number of the exposures. If these beads are due to the oscillatory discharge then possibly additional evidence may be had by photographing simultaneously the *negative* crest. This could be done by mounting two exactly similar canals with their attending equal electrostatic fields diametrically opposite in the apparatus, so that either in turn may serve as the cathode. The plate with this arrangement to be turned but a half revolution. The negative crests (corresponding to the troughs in Fig. 1) should appear on the plate as instantaneous photographs diametrically opposite to the corresponding photograph for the positive crests. Indeed, this point may be tested with the apparatus as originally constructed by giving the photographic plate a half turn then interchange the connections after which the turn is completed. A plate thus exposed should show negative crests, obviously not simultaneously with the positive crests, but negative crests due to oscillations accompanying a series of later discharges, and, so far as comparing the position of the negative crest with the positive trough is concerned, should answer equally well.

The second half of Fig. 13 was taken under the above conditions. It shows that cathode rays *do proceed* from the anode. Their presence and position may be accounted for by the negative crests of the damped oscillatory discharge. In this photograph they did not, however, accompany each discharge, but only about every fourth one, though careful measurements show that the groups that are recorded correspond in general to the troughs in the first half.

In Fig. 14 the static machine was replaced by the 8 inch Leeds induction coil, the vacuum was rather low, and X was made 1,800 volts (see Table I.). On this plate the negative crests appeared in great numbers due in part to the plate being turned more slowly in the second half. For the most part their positions correspond to a trough in the first half, as may be seen by the arc drawn on the photograph. It seems strange, however, that this photograph shows no negative crests corresponding to the first trough. In the next, Fig. 15, X was made 3,000, otherwise the conditions were the same as in the preceding photograph. In this negative crests appear in the second half corresponding to two troughs in the first half.

In the last photograph exposed, Fig. 16, the tube was again inserted. The vacuum though not recorded was high. In turning the plate it was halted twice, possibly for one or two seconds, in each half turn. Again the points appearing in the second half correspond to carriers having a lower velocity than in the first half. In comparison with Figs. 4 and 5 it is evident that the vacuum was too high, since apparently only the first positive and first negative group electrons were formed.

Conclusion.

It appears from the photographs reproduced in this paper that in most cases the beaded effect of the cathode ray line may be accounted for by the oscillatory character of the electric discharge. However a number of the photographs show beads whose spacing along the cathode line is not in agreement with that that should follow for damped oscillations. These may be due to ionization or secondary effects, or possibly due to group velocity electrons given off by the cathode. The position of the cathode seems to have but little or no effect upon the general character of the beads.

The strongest, and in some respects the most convincing evidence pointing to the oscillatory discharge as the origin of the beads is furnished by the photographs showing the negative crests. These crests in most every instance correspond to the troughs in the beaded line as shown in Figs. 13, 14, 15, and 16.

Admitting that the evidence submitted is sufficient to show that an oscillatory electric discharge under proper conditions (conditions which were met in a number of the foregoing photographs) results in a beaded cathode ray line, it seems that we have here a possible explanation of the beading of J. J. Thomson's molecular lines.[1] This conclusion, it seems to me, follows naturally because of the intimate relation that exists between the cathode rays and the positive rays which form the molecular line.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
March, 1913.

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[1] Philosophical Magazine, August, 1912, p. 237.

AN ELECTRIC CONVERTER.

By Wm. I. Book.

THIS paper describes a new method of producing electric oscillations of high frequency from a direct-current source. The apparatus is, therefore, called an electric converter.

In this method of producing electric oscillations the primary and secondary oscillating circuits are arranged in the same manner as they are for producing electric oscillations with the Duddell arc, and with the Poulsen arc. But the converter differs much from all other methods previously used to produce continuous electric oscillations.

Description of Apparatus.

The converter consists of a powerful electro-magnet with heavy tubular pole pieces, *a*, about 7.6 cm. in diameter. (See Fig. 1.) The walls of these pole pieces are reamed out, or tapered, at the end to a thickness of about 0.45 cm. Fitted on the end of each of these pole pieces is a fiber ring, *b*, about 10 cm. in outer diameter. To this fiber insulation is attached a copper (cathode) ring, *r*, about 5.6 cm. in inner diameter (to be described below). One of the tubular pole pieces is filled with a plug of fiber, *c*. A brass rod, *d*, neatly fits into a longitudinal hole through the center of this fiber plug. This rod is thus insulated from the pole pieces. There is fastened to the end of this rod by means of a machine screw a zinc or carbon (anode) disc, *e*, about 5.4 cm. in diameter. The faces of the fiber rings, mentioned above, project slightly beyond the ends of the pole pieces, making sockets into which are fitted discs of mica, *g*, over the ends of the pole pieces. These mica discs with the fiber rings insulate both the anode disc and the cathode ring from the pole pieces.

If a difference of potential of approximately 500 volts is impressed across the gap between the anode disc and the cathode ring, under the proper conditions, a spark or discharge will take place across the gap. Now if there is a current in the coil of the electro-magnet there is a powerful magnetic field between the poles of the magnet; the lines of force of the magnetic field passing chiefly through the gap between the anode disc and the cathode ring. The direction of the spark, therefore, is perpendicular to this magnetic field, and, in accordance with the fundamental principle which underlies the action of an electric motor, there is a force action on it perpendicular to both the magnetic field and the direction of the spark discharge. This causes the discharge to move around and around the circular gap between the anode disc and the cathode ring. But either the anode disc or the cathode ring must have a rough surface in order to obtain the conditions necessary to produce oscillations in an oscillatory circuit shunted about the spark-gap. It was found best to put a regularly roughened surface on the cathode ring. Different methods were tried for producing this regularly roughened surface. The simplest and most successful method tried was carefully to wind a soft copper wire of, say, No. 16 gauge on a ring made of No. 10 or No. 11 gauge wire. This wire-wound ring, *r*, was then soldered into a circular hole cut in a sheet of copper, this sheet of copper serving not only as a conductor to which the line from the negative brush of the dynamo is attached, but also as a heat radiator for the cathode ring, thus keeping it reasonably cool.

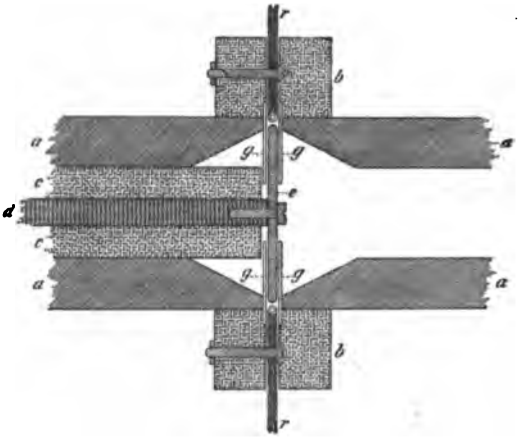

Fig. 1.

CONNECTIONS OF APPARATUS.

In Fig. 2, there is shown a general diagram of the connections of the apparatus. The source of difference of potential used, (E), was two ¼ horse-power 500 volt D.C. dynamos joined in parallel. R_0 is a variable resistance consisting of a bank of carbon filament lamps in series with a slide-wire contact resistance capable of varying the main current from about 1/10 of an ampere to about 1 ampere. I_0 is a direct current milliammeter with which to measure the current in the main circuit. L_0 is a choke coil. The high tension side of an ordinary electric light transformer was used for the choke-coil. *G* is the gap between the anode disc and the cathode ring. C_1 is a variable capacity in oil. C_2 is a similar capacity in the secondary oscillating circuit. L_1 is the primary of a closely wound induction coil. L_2 is the secondary of this coil. I_1 is a hot wire ammeter with which to measure the current in the primary oscillating circuit. R_2 is a variable resistance consisting of a bank of carbon filament lamps.

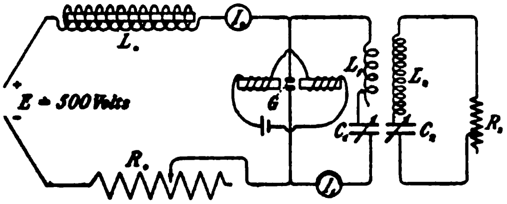

Fig. 2.

Theory and Principles of the Action of the Spark-Gap.

When the apparatus is connected as shown in the diagram, Fig. 2, and when the proper conditions are produced for the spark discharge to take place, the spark will pass around and around in the gap between the inside disc and the outside regularly roughened or notched ring. Because of the notches or grooves in the outside ring the sparking distance alternates rapidly from a given minimum to a given maximum as the discharge passes around the gap; and, therefore, the resistance of the gap likewise varies with this varying length. The function of the choke coil in the main circuit now appears. It serves to maintain a nearly constant supply of energy through the gap and the primary oscillating circuit shunted around the gap. When the spark is passing between the inside disc and a *ridge* on the outside ring the resistance across the gap has a minimum value, but when the spark is passing between the disc and a *groove* in the outside ring the resistance of the gap is a maximum. There will, therefore, be a rapdily alternating *flow* and *ebb* of energy into the primary circuit,—at each high resistance in the gap a *flow*, at each low resistance in the gap an *ebb*. Since the primary oscillating circuit has a natural frequency of its own, it would seem that the oscillations in this primary circuit for a given set of conditions will have an increased amplitude,—and, therefore, a greater amount of energy will be in the primary circuit,—when the natural frequency of the primary oscillating circuit is an integral multiple of the frequency of the flow and ebb of energy into this circuit due to the alternating higher and lower resistances in the spark gap.

A number of variables however enter into the investigation of these circuits and the complete determination of their inter-relation is not as simple a problem as at first it seems to be. The D.C. voltage impressed across the gap, the amount of current in the main circuit, the average length of the spark gap, the number of ridges and grooves in a given length of arc of the spark gap circumference, the intensity of the magnetic field through the gap; these are some of the quantities to be investigated.

OBSERVATIONS AND DISCUSSION.

The spark-gap may vary in mean length with different conditions from 0.2 mm. to 2.5 mm. It will be observed at once that with a spark gap of this length it is necessary to start the spark discharge by some mechanical means. This is done by pushing a small wire into a groove in the fiber next to the cathode ring so that the wire touches both the inside disc and the outside ring. This closes the main circuit. The wire is immediately withdrawn, thus starting the spark discharge.

The curves of Fig. 3 show the result of using different lengths of spark gap. The curve marked "Zn_i" shows the variation of current in the primary oscillating circuit with a change in the length of the gap when zinc was used for the anode disc. The curve marked "C_i" shows the same thing for carbon as the anode disc. On the same chart are shown

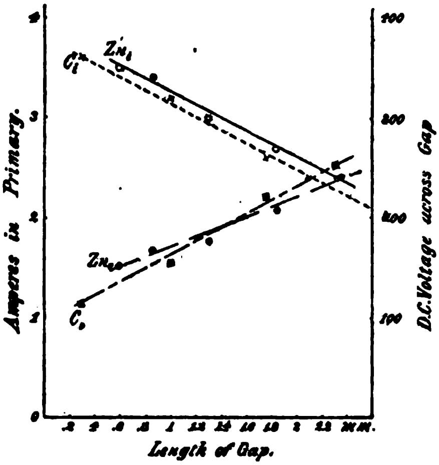

Fig. 3.

Variation of current in primary with change of spark-gap length. Variation of voltage across gap with change of spark-gap length. Field = 4,500 gauss, I_0 = 0.65 amp., C_1 = 3.4×10^{-3} M.F.

two curves which illustrate the variation of D.C. voltage across the gap with a change of spark gap length. These curves are marked "Zn_v" and "C_v." For best results the spark gap should be from 0.4 mm. to 1.5 mm. in length. These curves seem to indicate that zinc or carbon may be used for the anode disc with approximately the same results. Brass and aluminium were tried with practically the same success.

The study of the effect of a varying field upon the current in the primary oscillating circuit follows. To get the relation between these quantities it is necessary first to know the relation between the current in the coil to produce the magnetic field across the gap, and the field itself. This relation was determined by plotting a curve with the current in the field coil, measured in amperes, as abscissas and with the field, measured in gausses, as ordinates. From this curve it was easy to note the field through the gap corresponding to any current in the field coil. The method used to determine the field strength was the method of the bismuth spiral; the pole pieces being kept at the same distance from each other as they are when the anode and cathode parts are between them, *i. e.*, at a distance of approximately 0.7 cm.

If, now, the spark discharge be started and all the variable quantities in both the main circuit and the oscillating circuits be kept constant, but the field be increased gradually, the current in the primary oscillating circuit will also increase. It does not, however, increase as a straight line function, but rises to a maximum above which an increase of field will not further augment it. If the field is increased considerably beyond the value which, for a given set of conditions, will give the maxi-

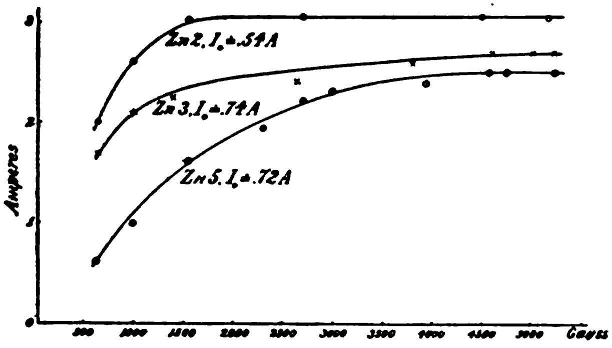

Fig. 4.

Current curves with change of field across gap. $C_1 = 3.4 \times 10^{-3}$ M.F., $V_1 = 125$ to 230 volts, depending upon length of gap. $\lambda_1 = 330$ m.

mum current in the primary oscillating circuit the spark discharge sputters or becomes noisy and the energy in the oscillating circuit is decreased rather than increased. In Fig. 4 are shown three characteristic curves illustrating the above mentioned result. The readings for the curve marked "*Zn* 2" were obtained when a spark gap of 0.85 mm. was used. The spark gap for the curve "*ZN* 3" was 1.3 mm. long, and that for the curve marked "*Zn* 5" was 2.3 mm. in length. The explanations of this result that have suggested themselves to the writer are not entirely satisfactory to him and are reserved for further verification.

The curve of Fig. 5 marked I_1 shows the increase of current in the primary oscillating circuit with a gradual increase of the capacity in that circuit. The curve marked I_0 shows the amount of current in the supply circuit corresponding to these different amounts of capacity and current in the primary oscillating circuit. The readings for the curves were taken with the magnetic field across the gap maintained at about 4,500 gausses.

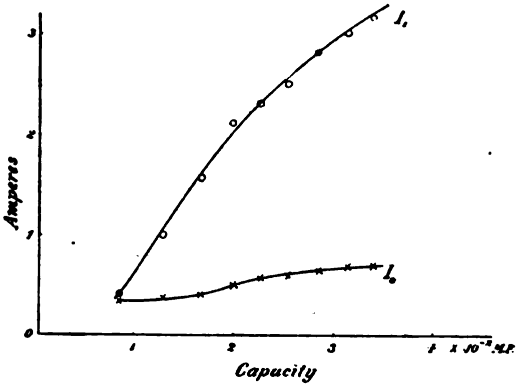

Fig. 5.

Supply circuit and oscillatory circuit currents with change of primary capacity.

To get the maximum current in the primary oscillating circuit for a given amount of capacity in this circuit the current in the main, or supply circuit must not be too large. When there is too much current in the main circuit the spark discharge sputters and is irregular, and thus little energy gets into the oscillating circuits. But when this condition is present, if the supply current is gradually decreased the gap runs more and more smoothly, and the current in the primary oscillating circuit gradually increases. If the supply current is still gradually decreased by means of the variable resistance in the main circuit the current in the oscillating circuit continues to increase until it comes always to a maximum value for the given capacity in the circuit. If the supply current is decreased yet a trifle the spark suddenly stops—"blows out." This is a very characteristic phenomenon of the converter. It seems to indicate that as the energy in the oscillating circuit becomes greater and greater a condition is reached where the back E.M.F. impressed across the gap due to the oscillations in this circuit is sufficient to reduce the D.C. voltage across the gap to too low a value to maintain the spark discharge.

The number of notches per unit length of arc of the spark gap circumference is an important factor in determining the amount of energy that is transformed in the oscillating circuits. A very large number, say 25 per centimeter of arc, is of no advantage, but rather of a disadvantage. If the number be too large the spark discharge, or arc, spreads over several of them, and thus a regular and considerable rise and fall of the spark gap resistance is not obtained. On the other hand if the number of notches be too few then the number of pulses per unit of time is not sufficient, with a low field across the gap, to maintain the oscillations in the primary circuit. However, with only 54 notches in the entire circumference of the gap the current in the primary increases very rapidly as the magnetic field across the gap is increased. The best results were obtained with a cathode ring made with about 10 notches per centimeter of arc.

Among the observations made in connection with the secondary circuit one notable fact was observed. It was frequently noticed that when the gap was in operation with slightly too much current in the supply circuit and when the secondary was not tuned to the primary, the tuning of the secondary to the primary produced the condition in the gap which would be obtained by gradually decreasing the current in the supply circuit; *i. e.*, the spark discharge becomes more regular and quiet and the current in the primary increases. If the gap is already acting smoothly before the secondary is tuned to the primary an attempt to tune it will cause the spark to "blow out."

APPLICATION.

A very interesting application of this new converter occurs in wave-telegraphy. The writer has at different times successfully signalled by means of it to a private wireless station three city blocks distant. These signals were very distinctly heard at stations at a distance of from three to five miles from the Randal Morgan Laboratory of Physics where this research was pursued.

There are several ways to produce the signals with this apparatus. One method is to join in series with the secondary circuit (which is the antenna circuit here) a suitable resistance of, say, carbon filament lamps and shunt this resistance with the signaling key. Upon pressing the key to produce a signal the resistance is shunted and the energy in the secondary is radiated through the antenna instead of being used to heat the resistance. Another method is to join in parallel with the antenna circuit a secondary which can be tuned to the primary. These two circuits have placed in them a double-action key. When this secondary circuit is closed it diverts the energy from the antenna circuit. When the key is pressed to produce a signal the tuned secondary circuit is broken. The energy then "flows" into the antenna circuit and is radiated by it.

It is the confident belief of the writer that this method of producing continuous high frequency oscillations will succeed not only in wireless telegraphy but also in wave-telephony.

SUMMARY.

1. A result of this research is that an electric converter to produce continuous electric oscillations of high frequency has been constructed which applies the fundamental principle of the electric motor. A gas serves as the conductor. A radial spark discharge takes place through air at right angles to an intense magnetic field; and in accordance with the electro-dynamical principle involved there is a force action on the spark perpendicular both to the direction of the magnetic field and to the direction of the spark discharge, causing the spark to move rapidly around in a circular gap.

2. An advantage of this converter consists in the fact that the spark discharge takes place in air instead of in some other gas such as hydrogen.

3. To produce the electric oscillations in the oscillatory circuit the circular spark gap should be regularly notched with about 10 notches per centimeter of arc.

4. The length of the spark gap may be from 0.4 mm. to 2.5 mm.

5. An increase of the magnetic field across the gap increases the energy in the oscillatory circuit but not in constant ratio with the increasing field.

6. By increasing the capacity in the primary oscillatory circuit the oscillating current is rapidly augmented, while the increase in the supply current to make possible such increase of capacity is small.

7. Too large a supply current decreases the energy of the oscillatory circuit. For a given set of conditions if the supply current be gradually decreased the oscillating current increases until a condition is reached where further decrease of supply current causes the spark to suddenly stop.

8. This type of electric converter is well adapted to use in wave-telegraphy.

In conclusion I wish to thank Professor A. W. Goodspeed, director of the Randal Morgan Laboratory of Physics, for placing at my disposal the facilities of the laboratory which made possible this investigation. I also wish to acknowledge my indebtedness to Dr. R. H. Hough for much valuable assistance, and for suggesting to me the fundamental idea from which this research developed.

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University of Pennsylvania.

THERMAL CONDUCTIVITY OF AIR AT LOW PRESSURES.

By A. Trowbridge.

IN the course of an investigation, still in progress, which involves the use of bolometers enclosed in a vacuum, irregularities in the equilibrium temperature of the bolometers were noted which were too large to permit a continuance of the work. It was obvious that the temperature variations were caused by variations in the pressure of the gas residues contained in the vacuum but as these pressure changes were found not to be wholly due to leaks and seemed to be unavoidable under the conditions of the original investigation, it was decided to make a separate study of the effect of pressure on the equilibrium temperature of a bolometer in order to ascertain whether or not there were any pressure at which the rate of change of the temperature with the pressure is a minimum.

The results of this subsidiary research seem to the writer to be of sufficient importance to warrant the publication of them separately especially as the main investigation of which this is a "by-product" will not soon be completed.

A body heated in a vacuum loses energy by conduction in its own material; by conduction due to the gas residues; by gas convection and by radiation. For small differences of temperature between the body and the enclosure the radiation may be taken to be proportional to this temperature difference and to depend in addition on the geometry of the system and on the nature of the radiating surfaces. For pressures of less than one tenth of a millimeter of mercury the energy loss by gas convection may be neglected in practice. The loss by conduction through the material of the body itself may be calculated from a knowledge of the thermal conductivity of the material and its geometry and by a proper choice of dimensions may be rendered small compared to the losses by other means.

The remaining mode of energy loss (gas conduction) is the only one which can depend primarily on the gas pressure.

It is known from the theoretical work of Maxwell and from the experiments of Kundt and Warburg that the thermal conductivity of a gas should be independent of the pressure so long as this is not too small and it is known that at very low pressures the conductivity is a function of the pressure.

M. v. Smoluchowski[1] has accounted for the latter fact on the principles of the kinetic gas theory by the aid of the assumption that while the "internal" conductivity is independent of the pressure there exists at the boundary wall a temperature discontinuity caused by imperfect thermal interchange and that this, itself a function of the pressure, plays an ever-increasing rôle in determining the energy flow as the pressure is reduced. When the pressure is so low that the mean free path of the gas particle is more than the distance which separates the body from its enclosure the "internal" conductivity no longer determines the energy flow even in part but the "external" conductivity is all-important and this M. v. Smoluchowski shows to be theoretically proportional to the gas pressure.

The results for the conductivity of air at low pressures obtained by calculation from the equilibrium temperatures of bolometers were in such good accord with the above theoretical considerations that it was decided to test them more accurately than had been possible in the preliminary experiment.

With this purpose the bolometer was abandoned for a platinum wire 30 cm. long and 0.005 cm. in diameter wound into a spiral and coated with platinum-black. This was mounted in the center of a glass bulb about 5 cm. in diameter connected to a Gaede molecular pump provided with a McLeod gauge capable of measuring gas pressures down to 1.5×10^{-6} mm. A tube containing cocoanut charcoal for use with liquid air to produce a vacuum free from mercury vapor was also connected with the tube containing the platinum spiral.

The spiral wire was sufficiently long in comparison to its diameter to make the energy loss by end-conduction negligible with respect to the losses by radiation and by gas conduction. The spiral formed one branch of a Wheatstone bridge, two of the remaining three branches of which were manganin coils of 1,000 ohms each. Opposite to the spiral was a manganin coil whose resistance was very slightly greater than that of the spiral and this coil was shunted with a variable high resistance so that the combined resistance of the branch could be made exactly equal to the resistance of the spiral.

After having determined the temperature coefficient of resistance of the platinum spiral in the usual manner it was found that the temperature of the spiral was very accurately proportional to the square of the current flowing in it provided the temperature rise of the spiral was not more than 20 to 30 degrees centigrade and provided the pressure of the gas in the bulb containing the spiral is maintained constant. This is to be expected since the rate of energy input is proportional to the square of the current and the energy outflow is proportional to the temperature difference between the body and the wall for small differences of temperature. The slope of the straight line connecting temperature rise and the square of the heating current depends only on the gas pressure in the enclosure, being in fact great for low pressures and small for high pressures.

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[1] Annalen der Physik, 35, p. 983, 1911.

It would seem thus that the slope of the temperature-(current)^2 curve might be brought into quantitative relation with the pressure corresponding to this slope and thus a law relating the gas conductivity with the pressure might be obtained.

This expectation has been fulfilled as a result of the observations reported further on.

The following table gives the results of a series of observations obtained with a blackened platinum wire in a glass enclosure which was maintained at a temperature of zero degrees centigrade by being kept in a Dewar flask containing cracked ice. In column 1 are tabulated the values of the gas pressure[1] in thousandths of a mm. of mercury. In column 2 are given the slopes of the temperature-(current)^2 function. Column 3 contains the reciprocal of the square of the values in column 2. Column 4 contains the values of column 3 diminished by the reciprocal of the square of the slope at zero pressure (this value was obtained by exterpolation). The last column contains the ratio of the values in column 4 to the corresponding values in column 1. The values in columns 2 to 4 inclusive are in arbitrary units.

Although there is a wide variation in the values in columns 1 and 4, column 5 shows a very fair degree of constancy.

In order to draw conclusions from this experimental result it is necessary to interpret the physical significance of the quantities $(1/s)^2$ and $(1/s_0)^2$.

If t represent the difference in temperature between the spiral and its enclosure when the current J flows we have the change in resistance of the spiral given by $r_t = r_0(I + \alpha t)$ where α is the temperature coefficient of the resistance of the material of which the spiral is made.

For small values of t it was found experimentally that $r \sim J^2$ or $r = sJ^2$ or $s = r/J^2$ where s is the slope given in column 2 of the table; hence $t = J^2s/r_0\alpha$. If λ be the loss in calories per second per unit length per degree difference in temperature due to gas conduction and σ be the loss due to radiation expressed in the same units and if the losses due to convection and to conduction in the material of the wire be negligible the total loss from the wire when it is t degrees centigrade above its surroundings ($(\lambda + \sigma)t$) must be equal to the energy supplied by the current ($0.239 J^2 r_0/e$).

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[1] The pressures are not those at which observations were taken but are values taken from a smooth curve laid through the observation points. These latter were all so close to the smooth curve that the values in column 1 practically represent observation points and are more convenient for calculation.

TABLE I.

I. P. in Mm. Hg.	II. Slope.	III. $\left(\frac{1}{\text{Slope}}\right)^2$.	IV. $\left(\frac{1}{S}\right)^2 - \left(\frac{1}{S_0}\right)^2$.	V. $\left(\frac{1}{S^2}\right) - \left(\frac{1}{S_0}\right)^2 + p$.
10×10^{-3}	1,670	36×10^{-8}	20×10^{-8}	20×10^{-6}
20	1,355	54.8	38.8	19.9
30	1,155	75.5	59.5	19.8
40	1,000	100	84.0	21.0
50	893	123	107	21.4
60	820	146	130	21.6
70	770	169	153	21.8
80	735	185	169	21.1
90	695	207	191	21.2
100	663	228	212	21.2
110	629	252	236	21.4
120	610	269	253	21.1
130	591	286	270	20.8
140	571	306	290	20.7
150	552	327	311	20.7
160	538	346	330	23.0
170	523	365	349	23.5
180	511	383	367	22.0
190	500	400	384	21.0
200	485	424	408	22.0

Thus $t = 0.239 J^2 r_0/(\sigma + \lambda)l$ but since $t = J^2 s/r_0 \alpha$

$$(\sigma + \lambda) = \frac{0.239 r_0^2 \alpha}{ls} = k\frac{1}{s};$$

$$\therefore \quad \frac{1}{s^2} = \frac{1}{k^2}(\sigma + \lambda)^2.$$

Thus at pressure p

$$\left(\frac{1}{s_p}\right)^2 = \frac{1}{k^2}(\sigma + \lambda_p)^2 \tag{1}$$

and at pressure 0

$$\left(\frac{1}{s_0}\right)^2 = \frac{1}{k^2}(\sigma + \lambda_0)^2 \tag{2}$$

and the constancy of the values in column 5 of the table indicates that

$$(\sigma + \lambda_p)^2 - (\sigma + \lambda_0)^2 = k'p. \tag{A}$$

If we assume that at pressure zero the gas conductivity is also zero we have $\sigma^2 + 2\sigma\lambda_p + \lambda_p^2 - \sigma^2 = k'p$ or $2\sigma\lambda_p + \lambda_p^2 = k'p$. For very low pressures λ_p is small compared to σ for σ is independent of the pressure and hence in this case λ_p is proportional to the pressure. This is a result at which v. Schmoulouski arrived in his paper cited above.

If on the other hand the pressure is great the quadratic form of the function λ_p allows a practical independence of the pressure as Maxwell showed should be the case at high pressures. Thus equation A which satisfactorily represents the observations made with a blackened platinum wire in an enclosure of glass at constant temperature is in agreement with theoretical conclusions both at very low and at very high pressures.

In the former of the two cases the conductivity is proportional to the number of molecules present in unit volume. This is what we might expect if each molecule moved from the wire to the wall without colliding with its neighbors since this could only happen if the mean free path of the molecule were large in comparison to the distance between the wire and the wall, *i. e.*, at low pressures.

In the latter of the two cases the conductivity may be independent of the pressure because while the number of molecules in unit volume increases with the pressure the mean free path decreases in like amount so that the energy transfer may be independent of the pressure if the distance between the wire and wall be a great many times the mean free path.

It will be seen that the radiation σ may be calculated from equation (2). It may also be calculated as follows if we assume the wire to be a black body, cylindrical in form, of radius R and length 1 cm. The radiation loss per second of such a body is $2\pi lRA(T^4 - T_0^4)$ where A is the constant of the Stefan-Boltzmann law and T and T_0 are the absolute temperatures of the wire and the enclosure respectively. If the difference of these temperatures is small the loss may be expressed by $8\pi RT_0^3ltA$ and the loss per unit length per degree difference in temperature between wire and wall is

$$\sigma = 8\pi RAT_0^3. \tag{3}$$

(Since A is expressed in calories per sq. cm. per sec. σ will be expressed in calories per sec. per cm. length.)

The value calculated from this formula is 16.2×10^{-7} while that calculated from the data contained in the table is 20.3×10^{-7}. This difference is in part due to the fact that the area of the blackened wire is greater than that of the bare wire whose dimensions were used in the calculations by means of equation 3. As a further test as to whether I/s_0

is proportional to σ a series of observations was taken with the enclosure at 26 degrees centigrade. It was found that the value of the quantity k in equation A was unchanged although the value of $(I/s_0)^2$ was increased from 16×10^{-8} to 28×10^{-8}. The square root of the ratio of these two numbers is the ratio of the corresponding values of the radiation constants σ. Thus $\sigma_{26}/\sigma_0 = 1.32$. By equation 3 this ratio should be equal to the ratio of the cubes of the absolute temperatures, which is 1.31.

On the whole the calculations based on the assumption that the wire and the enclosure are black bodies are in very fair accord with the facts, but equation (A) is by no means restricted to the case of black bodies. In fact the equation shows that in the experimental determination of the gas conductivity it is advisable to employ a poor radiator so that σ may be small compared to λ.

With the object of testing further the validity of equation (A) experiments were undertaken with an unblackened spiral of platinum wire. The experimental procedure was altered as follows: Instead of observing the change of the resistance of the spiral for two different heating currents J_1 and J_2 at every pressure p the current J_p which must needs flow in order to raise the temperature an assigned amount was observed for every gas pressure.

Since $t = J^2 s_p / r_0 \alpha$ if t be kept constant $s_p \backsim 1/J_p^2$ and by equations (1) and (2) $J_p^4 \backsim (\sigma + \lambda_p)^2$ and $J_0^4 \backsim (\sigma + \lambda_0)^2$. Thus for equation ($A$) to be true $J_p^4 - J_0^4$ must be proportional to the pressure p.

In practice the Wheatstone bridge which contained the spiral as one of its branches was always kept in balance so that the spiral was about 10 degrees C. hotter than its surroundings. To accomplish this the resistances of the other three branches of the bridge were maintained constant and the current was adjusted to the proper value for each gas pressure at which observations were taken. This current was measured

Table II.

Pressure in Mm.	J_p^4	$(J_p^4 - J_0^4)$	$(J_p^4 - J_0^4) + p$
16×10^{-3}	12.8×10^{-9}	12.3×10^{-9}	7.7×10^{-7}
9.2×10^{-3}	7.27×10^{-9}	6.77×10^{-9}	7.4×10^{-7}
7.6×10^{-3}	6.45×10^{-9}	5.95×10^{-9}	7.8×10^{-7}
7.4×10^{-3}	5.96×10^{-9}	5.46×10^{-9}	7.4×10^{-7}
5.2×10^{-3}	4.02×10^{-9}	3.52×10^{-9}	6.8×10^{-7}
4.86×10^{-3}	3.98×10^{-9}	3.48×10^{-9}	7.2×10^{-7}
3.2×10^{-3}	2.48×10^{-9}	1.98×10^{-9}	6.2×10^{-7}
2.5×10^{-3}	2.40×10^{-9}	1.90×10^{-9}	7.6×10^{-7}

on a Weston mil-ammeter. This method of observation is, of course, not so accurate as that first employed as it involves the reading of a deflection instrument but it has the advantage of permitting rapid measurement. For some time past the writer has employed a heated platinum spiral in the manner just described as a substitute for the McLeod gauge in the pressure range below one one-thousandth of a millimeter of mercury and has found it possible to take about twenty pressure measurements with the spiral in the time required to take a single observation with the McLeod gauge. The following table includes the results of a characteristic series of observations taken by the last-described method:

As will be seen by comparison with Table I. the constancy in the last column is here not quite so satisfactory as in the case of the results obtained by use of the first method. This is undoubtedly due in part, as already mentioned, to the use of the mil-ammeter, and in part also to the fact that the gas pressures employed were much lower than in the first series and hence were less accurately determined by means of the McLeod gauge. It is evident however from a study of both the tables that within the limit of probable error the equation (*A*) is satisfied and that at low pressures the gas conductivity is proportional to the number of gas molecules present in unit volume.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
June, 1913.

EXTENSION OF MAXWELL'S SERIES FORMULA FOR THE MUTUAL INDUCTANCE OF COAXIAL CIRCLES.

By J. G. Coffin.

THE most important formula for the mutual inductance of coaxial circles is the exact formula in elliptic integrals given by Maxwell:[1]

$$M = 4\pi\sqrt{Aa}\left\{\left(\frac{2}{k} - k\right)F - \frac{2}{k}E\right\}, \tag{1}$$

in which A and a are the radii of the two circles, d is the distance between their centers, and

$$k = \frac{2\sqrt{Aa}}{\sqrt{(A+a)^2 + d^2}} = \sin\gamma.$$

F and E are the complete elliptic integrals of the first and second kind, respectively, to modulus k.

He also obtained an expression for the mutual inductance between coaxial circles in the form of a converging series which is sometimes more convenient to use, but has the especial importance of being integrable over the cross sections of coaxial coils thus giving rise to many valuable formulæ. It is thus seen to be a formula of fundamental importance. Maxwell however carried the series to terms of the third degree in c/a and d/a only. A and a are the radii of the two circles, $c = A - a$, d is their distance apart. His formula includes only the terms of the third degree of the following one.

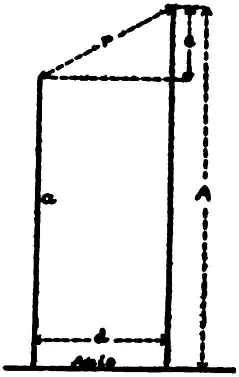

Fig. 1.

$$\begin{aligned}M = 4\pi a\Bigg\{\log\frac{8a}{r}\bigg(1 + \frac{c}{2a} + \frac{c^2+3d^2}{16a^2} - \frac{c^3+3cd^2}{32a^3} + \frac{17c^4+42c^2d^2-15d^2}{1{,}024a^4}\\ - \frac{19c^5+30c^3d^2-45cd^4}{2{,}048a^5} + \cdots\bigg) - \bigg(2 + \frac{c}{2a} - \frac{3c^2-d^2}{16a^2} + \frac{c^3-6cd^2}{48a^3}\\ + \frac{19c^4+534c^2d^2-93d^4}{48\cdot128a^4} - \frac{379c^5+3{,}030c^3d^3-1{,}845cd^4}{480\cdot128a^5} + \cdots\bigg)\Bigg\}.\end{aligned} \tag{2}$$

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[1] Electricity and Magnetism, 4, p. 301, 1907.

E. B. Rosa and Louis Cohen[1] extended Maxwell's formula to terms of the fifth degree by expanding the terms of formula (1) in series and substituting them in it. Their result is formula (2). Nagaoka[2] confirmed this formula including terms of the fourth degree by means of an expansion of a formula due to him in the *q*-series of Jacobi.

Coffin[3] in order to deduce a formula for the self-inductance of a cylindrical coil deduced a formula equivalent to Maxwell's in which $c = 0$, that is, for equal circles, up to and including terms of the eighth degree, which gives with considerable exactness the mutual inductance of equal circles up to $d = a$. Coffin's formula is

$$\begin{aligned} M = 4\pi a \Big\{ \log\frac{8a}{d}\Big(1 + \frac{3d^2}{16a^2} - \frac{15d^4}{8\times 128a^4} + \frac{35d^6}{128^2a^6} - \frac{1{,}575d^8}{2\times 128^3a^8} + \cdots\Big) \\ - \Big(2 + \frac{d^2}{16a^2} - \frac{31d^2}{16\times 128a^4} + \frac{247d^6}{6\times 128^2a^6} - \frac{7{,}795d^8}{8\times 128^3a^8} + \cdots\Big). \end{aligned} \tag{3}$$

This formula has been amply verified in the form it is and in the form of an expression for the self-inductance of a cylindrical current sheet deduced from it, by many numerical calculations compared with numerical results deduced from absolute formulæ. In 1908 Havelock[4] deduced an expression for the mutual inductance of coaxial circles depending on certain definite integrals of Bessel functions which he expanded in series. His formula is

$$\begin{aligned} M = 4\pi\sqrt{Aa}\Big\{ \log\frac{8\sqrt{Aa}}{r}\Big[1 + \frac{3}{16}\Big(\frac{r^2}{Aa}\Big) - \frac{15}{1{,}024}\Big(\frac{r^2}{Aa}\Big)^2 + \cdots\Big] \\ - \Big[2 + \frac{1}{16}\Big(\frac{r^2}{Aa}\Big) - \frac{31}{2{,}048}\Big(\frac{r^2}{Aa}\Big)^2 + \cdots\Big]\Big\}. \end{aligned} \tag{4}$$

This formula is simpler for use than Maxwell's but it is not in a form suitable for integration. Rosa noticed however that when $A = a$ Havelock's formula reduces to Coffin's formula (3) and hence it may be extended as follows:

$$\begin{aligned} M = 4\pi\sqrt{Aa}\Big\{\Big[1 + \frac{3}{16}\alpha - \frac{15}{1{,}024}\alpha^2 + \frac{35}{128^2}\alpha^3 - \frac{1{,}575}{2\times 128^3}\alpha^4 + \cdots\Big]\log\frac{8\sqrt{Aa}}{r} \\ - \Big[2 + \frac{1}{16}\alpha - \frac{31}{2{,}048}\alpha^2 + \frac{247}{6\times 128^2}\alpha^3 - \frac{7{,}795}{8\times 128^3}\alpha^4 + \cdots\Big]\Big\}, \end{aligned} \tag{5}$$

where $r^2 = c^2 + d^2$, $a = r^2/Aa$.

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[1] Bulletin of the Bureau of Standards, 2, p. 364, 1906.

[2] Nagaoka, Phil. Mag., 6, p. 19, 1903.

[3] J. G. Coffin, Bulletin of the Bureau of Standards, 2, p. 113, 1906.

[4] Havelock, Phil. Mag., 15, p. 332, 1908.

It occurred to the writer that Rosa's extension of Maxwell's formula (2) might be confirmed and new terms deduced in the following manner. This will be especially valuable, as the confirmation will be by a method independent of both Maxwell's and Rosa's.

Since $A = a + c$

$$\alpha = \frac{r^2}{Aa} = \frac{d^2 + c^2}{(a + c)a} = \frac{d^2 + c^2}{a^2}\,\frac{1}{\dfrac{a + c}{a}} = (\eta^2 + \epsilon^2)(1 + \epsilon)^{-1},$$

$$Aa = (a + c)a = a^2(1 + \epsilon),$$

$$\sqrt{Aa} = a(1 + \epsilon)^{\frac{1}{2}},$$

$$\log \frac{8\sqrt{Aa}}{r} = \log \frac{8a(1 + \epsilon)^{\frac{1}{2}}}{r} = \log \frac{8a}{r} + \log (1 + \epsilon)^{\frac{1}{2}},$$

where $c/a = \epsilon$ and $d/a = \eta$.

With these substitutions Havelock's formula (5) becomes

$$\begin{aligned} M = 4\pi a \Bigg\{ \log \frac{8a}{r} \bigg(&(1+\epsilon)^{\frac{1}{2}} + \frac{3}{16}(\eta^2+\epsilon^2)(1+\epsilon)^{-\frac{1}{2}} \\ &- \frac{15}{1{,}024}(\eta^2+\epsilon^2)^2(1+\epsilon)^{-\frac{3}{2}} + \text{etc.}\bigg) \\ + \tfrac{1}{2}\log (1+\epsilon) \bigg(&(1+\epsilon)^{\frac{1}{2}} + \frac{3}{16}(\eta^2+\epsilon^2)(1+\epsilon)^{-\frac{1}{2}} \\ &- \frac{15}{1{,}024}(\eta^2+\epsilon^2)^2(1+\epsilon)^{-\frac{3}{2}} + \text{etc.}\bigg) \\ - \bigg(&2(1+\epsilon)^{\frac{1}{2}} + \frac{1}{16}(\eta^2+\epsilon^2)(1+\epsilon)^{-\frac{1}{2}} \\ &- \frac{31}{16\times 128}(\eta^2+\epsilon^2)^2(1+\epsilon)^{-\frac{3}{2}} + \text{etc.}\bigg). \end{aligned} \qquad (6)$$

By expanding the parentheses $(1 + \epsilon)^n$ by means of the binomial theorem and using the formula for the $\log (1 + \epsilon) = \epsilon - \frac{1}{2}\epsilon^2 + \frac{1}{3}\epsilon^3 - \frac{1}{4}\epsilon^4 + \cdots$, all of which are convergent for $\epsilon = c/a < 1$ or for $c < a$ we have obtained an extension of Maxwell's formula (2) up to and including terms of the eighth degree.

This extension confirms the coefficients of Rosa and Cohen's extension and may be expected to give formulæ on integration over large cross sections, which converge rapidly and are quite exact for values of c or of d almost as great as the radius a. This formula is as follows

$$
\begin{aligned}
M = 4\pi a \Bigg\{ \log \frac{8a}{r} \Bigg(& 1 + \frac{c}{2a} + \frac{c^2+3d^2}{16a^2} - \frac{c^3+3cd^2}{32a^3} + \frac{17c^4+42c^2d^2-15d^4}{1{,}024a^4} \\
& - \frac{19a^5+30c^3d^2-45cd^4}{16\cdot 128a^5} \\
A \quad & + \frac{89c^6+45c^4d^2-345c^2d^4+35d^6}{\overline{128}^2a^6} \\
B \quad & - \frac{109c^7-63c^5d^2-525c^3d^4+175cd^6}{2\cdot\overline{128}^2a^7} \\
C \quad & + \frac{8{,}921c^8-13{,}692c^6d^2-43{,}050c^4d^4+32{,}900c^2d^6-1{,}575d^8}{2\cdot\overline{128}^3a^8} \Bigg) \\
& - \Bigg(2 + \frac{c}{2a} - \frac{3c^2-d^2}{16a^2} + \frac{c^3-6cd^2}{48a^3} + \frac{19c^4+534c^2d^2-93d^4}{48\cdot 128a^4} \qquad (7) \\
& - \frac{379c^5+3{,}030c^3d^2-1{,}845cd^4}{480\cdot 128a^5} \\
A' \quad & + \frac{2{,}629c^6+12{,}045c^4d^2-17{,}445c^2d^4+1{,}235d^6}{30\cdot\overline{128}^2a^6} \\
B' \quad & - \frac{27{,}833c^7+71{,}169c^5d^2-225{,}225c^3d^4+50{,}575cd^6}{420\cdot\overline{128}^2a^7} \\
C' \quad & + \frac{\begin{matrix}5{,}204{,}309c^8+5{,}304{,}852c^6d^2-45{,}499{,}650c^4d^4 \\ \hfill +21{,}735{,}700c^2d^6-818{,}475d^8\end{matrix}}{840\cdot\overline{128}^3a^8} \Bigg) \Bigg\}.
\end{aligned}
$$

The terms marked A, B, C, A', B' and C' are the newly derived ones. Putting $c = 0$ this formula reduces to formula (3) as indeed it should, being based upon it.

Putting $d = 0$ we obtain a formula for the mutual inductance of coaxial circles in the same plane.

$$
\begin{aligned}
M = 4\pi a \Bigg\{ & \log \frac{8a}{c}\Bigg(1+\frac{c}{2a}+\frac{c^2}{16a^2}-\frac{c^3}{32a^3}+\frac{17c^4}{8\times 128a^4}-\frac{19c^5}{16\times 128a^5} \\
D \quad & +\frac{89c^6}{128^2a^6}-\frac{109c^7}{2\cdot 128^2a^7}+\frac{8{,}921c^8}{2\cdot 128^3a^8}-\cdots\Bigg) \\
& -\Bigg(2+\frac{c}{2a}-\frac{3c^2}{16a^2}+\frac{c^3}{48a^3}+\frac{19c^4}{48\cdot 128a^4}-\frac{379c^5}{480\cdot 128a^5} \\
D' \quad & +\frac{2{,}629c^6}{30\cdot 128^2a^6}-\frac{27{,}833c^7}{420\cdot 128^2a^7}+\frac{5{,}204{,}309c^8}{840\cdot 128^3a^8}-\cdots\Bigg)\Bigg\},
\end{aligned}
\tag{8}
$$

the terms in lines marked D and D' being new.

TEST OF THE FORMULA.

The ideal check on the new formula lies, of course, in its agreement with its derivation by independent methods such as those employed by Maxwell and by Rosa and Cohen.

But as these calculations were extremely laborious and the independent derivation by any other known method being more so, we have not undertaken to do this.

A numerical test is however of great value in such a case as this, for although it does not prove the correctness of any formula, it makes its essential correctness extremely probable.

We have made such a test for a few cases in which the true values of the mutual inductance were already known or in which they could be calculated by other absolute formulæ.

Example I.—Let $A = 25$ cm., $a = 20$ cm., $d = 10$ cm. (see Fig. 1). The value of the mutual inductance between these two circles has been calculated by Rosa and Grover[1] by means of Maxwell's absolute formula (1) to be $M = 248.7875$ cm.

Let M_n refer to the value of the mutual inductance between these circles calculated by means of the new formula (7) carried as far as and including terms of the nth degree. Then the following results have been obtained.

(Rosa and Grover) M_3 = ———— too large by 1 part in 1.750,
(Rosa and Grover) M_5 = 248.8006 cm., too large by 1 part in 19,000,
(New Formula) M_6 = 248.7892 cm., too large by 1 part in 125,000,
(New Formula) M_7 = 248.7865 cm., too small by 1 part in 250,000,
(New Formula) M_8 = 248.7877 cm., too large by 1 part in 1,250,000, or 4 parts in 5 million.

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[1] Bulletin Bureau of Standards, 8, p. 22, example 4, 1912.

The agreement is very satisfactory and the various results show the rapidity of the convergence of the formula.

The value of M computed by Havelock's formula (5) extended by means of the coefficients of formula (3) is for the same case:

$$M = 248.7873 \text{ cm.}$$

We at first thought that M_8 should agree exactly with the preceding value but on consideration have come to the conclusion that an *exact* agreement is not to be expected.

Example II.—In order to test the coefficients in formula (8), a special case of formula (7) in which d has been put equal to zero, we have calculated as follows:

$$A = 15 \text{ cm.}, \quad a = 10 \text{ cm.}, \quad c = 5 \text{ cm.}, \quad d = 0 \text{ cm.}$$

The exact value of this mutual inductance was derived correct to about 1 part in a million, by means of the absolute formula of Maxwell, employing the tables of

$$\log \frac{M}{4\pi\sqrt{Aa}} = \left\{\left(\frac{2}{k} - k\right)F - \frac{2}{k}E\right\}$$

given in the Bulletin of the Bureau of Standards.

Its value is

$$M = 162.69605 \text{ cm.}$$

As before let M_n refer to the value derived from (8) including terms of the nth degree, then:

$M_5 = 162.6816$ cm.; too small by 1 part in 19,000,

$M_6 = 162.6985$ cm.; too large by 1 part in 75,000,

$M_7 = 162.6943$ cm.; too small by 1 part in 100,000,

$M_8 = 162.6959$ cm.; too small by 1 part in 1,000,000.

This last result checks as nearly as the tables used will allow with the above value.

In both the above numerical cases, a very precise value would have been obtained omitting the eighth degree terms, if one half or one third of the correction due to the seventh degree terms had been used instead of its full value. There would always seem to be an improvement in doing this on account of the oscillatory character of these corrections.

RESUMÉ.

The important and integrable series formula of Maxwell for the mutual inductance between two coaxial circles has been extended by an independent method to include terms of the eighth degree. This is amply sufficient for the most precise calculations, in which c/a and d/a are not too near to unity.

The coefficients of the series including the fifth degree terms, as determined by another method by Rosa and Cohen, have been completely verified.

The correctness of the new formula has been tested by numerical examples and has been found to agree with absolute results to at least 1 part in 1,000,000, this being the limit of accuracy of the tables employed in the calculations.

Department of Physics,
The College of the City of New York,
March 22, 1913.

THE SIGNIFICANCE OF INTENSITY—SUM IN BINAURAL LOCALIZATION.

By G. W. Stewart.

In the various contributions on sound localization, numerous references have been made to the *difference in intensities* at the ears as an mportant factor in sound localization. That it is an important factor none can dispute, but there is no evidence that it is the most important intensity factor. The object of this paper is to consider the *sum of intensities* as a factor in practical localization. Obviously the relative importance of these two factors depends upon the conditions imposed in the experiments. If the head and the source of sound are stationary, then the intensity-difference and intensity-ratio are probably the only intensity factors. But if the observer is allowed to turn his head at will and if the sound is of sufficient duration, then he has the opportunity of comparing different intensity-sums with different positions of the head.

Theory.—In a previous theoretical investigation[1] the writer assumed that the apparent intensity of sound was the sum of the intensities at the two ears, phase not being considered, and accordingly curves were plotted showing the variation in this intensity-sum with different positions of the head. The character of the dependence of this variation upon wavelength was so different from that of intensity-difference and intensity-ratio and so unexpected withal that an experimental test was arranged to show whether or not the intensity-sum is a factor of importance. The results of the theoretical investigation of intensity-sum are reproduced in Fig. 1. Here the ordinates are relative values, unity at 0°, for the intensity-sums with different wave-lengths, and the abscissæ give the position of the head, 0° being the position with an ear toward the source, 90° the position with the source directly in front, and 180° with the other ear toward the source. The distance of the sound source is 477 cm. In the assumption involved in the theory, viz., that the head is a rigid sphere with the ears diametrically opposite, there is no distinction between front and rear and therefore the rotation of the head from 180° to 360° is secured by duplicating the curves shown in Fig. 1.

The results for wave-lengths of 240, 120 and 60 cm. are not surprising when one considers that with the shorter wave-lengths the head is more of an obstacle. That the curve for 30 cm. did not follow this general trend was a surprise. A check on these results is obtained from the results of Lord Rayleigh for a source at a great distance, for the variation in intensity in the shadow of the head with the source at 477 cm. is not greatly different from that with the source at a great distance.[1]

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[1] Stewart, Phys. Rev., XXXIII., No. 6, December, 1911, p. 467.

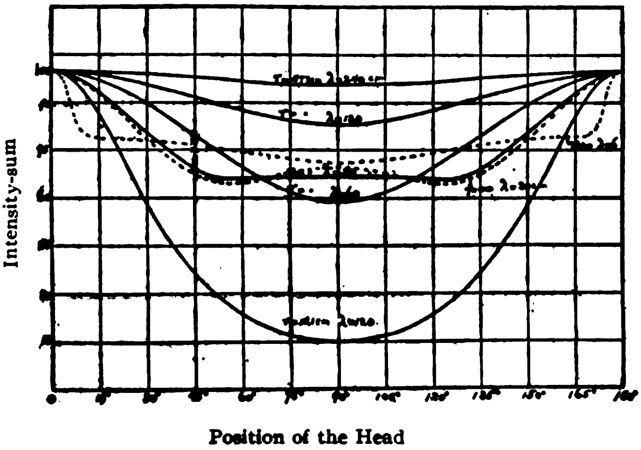

Fig. 1.

The intensity-sums obtained from Lord Rayleigh's results are represented in the figure by dotted lines. These additional curves also indicate that a curve obtained for a wave-length of 6 cm. would show a greater flattening. More theoretical curves would have been computed if the computations had not been very laborious or if there had been any doubt in regard to the conclusions that can be drawn.

The intensity-differences and intensity-ratios give curves of a very different character. Fig. 2 gives the results of such computations, utilizing the same values of intensities as before. The meaning of 0° and that of 90° are the same as before. It is obvious that these two sets of curves are similar in that the effect of changing the wave-length is a progressive one. In this respect they are not like the curves in Fig. 1. If the intensity-sum is of practical importance in the localization of sound, then the observer, when facing the source (90°), should have less difficulty in locating a source of wave-length 60 cm. than one of wave-length 30 cm. or 120 cm., for with the first named there is a greater variation of the intensity-sum with a given small rotation of the head, than with either the 30 cm. or 120 cm. wave-length. In other words, when the observer faces the source of sound, a given variation of intensity-sum is obtained with a less rotation of the head in the case of a wave-length of 60 cm. The curves do not show that 60 cm. is the "critical" wave-length. Additional curves would need to be plotted to get nearer the truth in this respect. But Fig. 1 does indicate that there is a critical wave-length. The question to be determined experimentally is whether or not this theoretical deduction can be observed in practice. If it can be observed then the intensity-sum must be an important factor in practical sound localization. But more than this. The curves in Fig. 2 indicate that

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[1] Stewart, loc. cit.

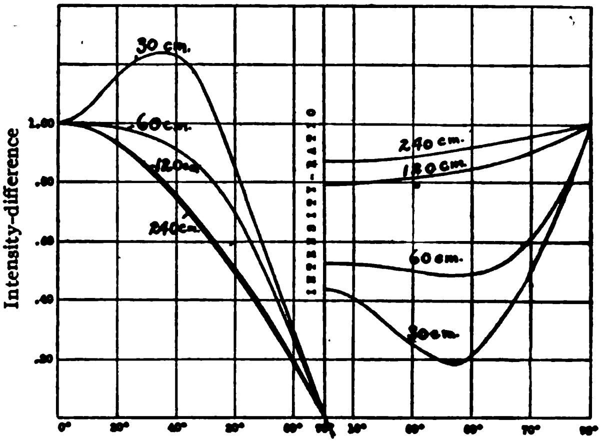

Fig. 2.

when the observer faces the source and rotates the head through a small angle, there is the greatest change with the smallest wave-length, since in each set of curves the slope for the 30 cm. curve is the greatest of the four at 90°. It would therefore seem that a search for this critical wave-length indicated in Fig. 1 would determine whether or not the intensity-sum theory is of greater importance under usual circumstances than either the intensity-difference or intensity-ratio theory. It seems to be a matter of common experience that very low or very high pitch tones are the most difficult to locate, but this is not sufficient to prove the point.

Experiment.—In a room with reflecting walls sound localization becomes a very complex problem. Experiments in the open air without reflecting surfaces are practically impossible. The results here recorded were obtained upon an open piece of ground thickly covered with grass. The sources of sound were tuning forks mounted upon resonators. No accurate measure of ability to localize was sought. The degrees of ability were graded in an arbitrary manner.

Any of the observers could without difficulty point directly to the source of sound, so readily were all the tones localized. When the observer, facing the source of sound 477 cm. distant, was asked to rotate his head back and forth and to indicate with a large pair of dividers the angle within which the sound seemed to be located with certainty, he found no serious difficulty in reaching a conclusion. The observer made his adjustment of the dividers with his eyes closed and the distance between the points of the dividers was taken as a measure of the angle within which the sound was definitely located. The angle varied with different tones. The results obtained are presented in Fig. 3.

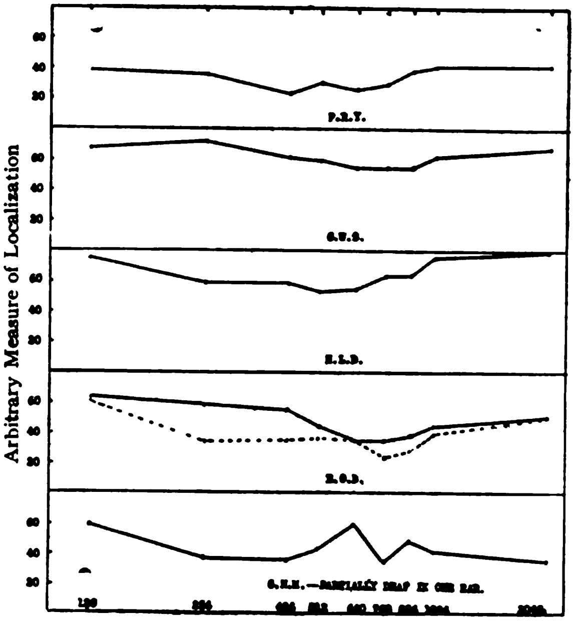

Fig. 3.

Nine forks were used and any order of presentation was carefully avoided. The results are averages of several observations for each fork. The observations of the first three are satisfactory. The observations of the fourth set, E. O. D., were taken upon windy days and were not satisfactory to the observer. The full line and the dotted line represent the results of experiments on different days. The fifth observer was partially deaf in one ear. In this case the curve shown is not obtained from a large number of observations but indicates in a general way the irregularity of his observations. The curve strengthens rather than weakens the conclusions derived from the other curves. The existence of a minimum is obvious for the percentage change in the arbitrary measure of angle of localization is very great. In fact in some cases the change is 100 per cent. of the minimum.

Although the experiments are somewhat crude and should be carried out with greater degree of accuracy, the results are unmistakable. The curves show that the frequency 512 to 640 is localized with the greatest accuracy, a confirmation of the theoretical deductions based upon the intensity-sum as a factor. That is, there is a critical wave-length in the neighborhood of 60 cm., frequencies 512 to 640. An inspection of the curves for intensity-differences and intensity-ratios shows that neither of these possible factors furnish an explanation of the experimental results, that indeed they would point toward very different results. The conclusion is that the intensity-sum is an important factor in practical localization where the observer can and does rotate the head in the interval of the sound duration. Indeed, the confirmation is so definite that one is inclined to believe that, in practical localization, the intensity-sum is the most important intensity factor.

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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

SOME MEASUREMENTS WITH THE MICROPYROMETER.[1]

By G. K. Burgess and R. G. Waltenberg.

THE micropyrometer[2] has been used for the exact determination of the melting points of the chemical elements of atomic weight from 48 to 59, using as calibration points Ni = 1,452, Pd = 1,549 and Pt = 1,755, and the calibration equation of the pyrometer lamp $\log c = a + b \log T$, where c = current and T = absolute temperature. Using samples from several sources, the following melting points were obtained in hydrogen: Cobalt, 1,478; iron (5 samples of which 3 electrolytic), 1,533; manganese, 1,260; chromium 1,520; vanadium, 1,720; and titanium, 1,795. Ni, Fe and Co were also checked in an Arsem furnace.

The melting points of Zr, Be, Y, Er, B, Th, U, etc., are under investigation, as also the measurement of the emissivities of the various elements by means of the micropyrometer. Alloying is shown not to affect the melting points of the metals except when there is chemical combination. Day and Sosman's values for the melting points of the salts: diopside, 1,391, and anorthite, 1,549, were also confirmed. Several hundred steels are also being examined. Some of the advantages of use of the micropyrometer are (1) small quantity of material required (0.001 mgr.); (2) speed, five to twenty minutes for a melting point determination at 1,700; (3) easy calibration, two points only required; (4) great range available, 600° to 3000° C.

SOME CHARACTERISTICS OF TOTAL RADIATION PYROMETERS.[1]

By G. K. Burgess and P. D. Foote.

ALTHOUGH the relation between the energy emitted by a black body and its temperature follows the law $J = \sigma T^4$, since the fraction absorbed by the radiation pyrometer is in general not a constant factor for all temperatures but rather of the form $f(T)$ we have for this type of pyrometer an equation which does not necessarily follow the fourth power law but has the form $E=aT^b$, where E is the electromotive force generated by the thermo-element, and a and b certain empirical constants, b varying from 3.5 to 4.2 with 17 instruments tested.

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[1] Abstract of a paper presented at the Washington meeting of the Physical Society, April 25 and 26, 1913.

[2] "A Micropyrometer," G. K. Burgess, Bull. Bureau of Standards, *9*, 475, 1913; Jl. Wash. Acad., *3*, 7, 1913.

The E.M.F. indicated by several Féry total radiation pyrometers showed a marked lag effect due to a slow heating of the couple. Frequently, as long an exposure as ten minutes is required before the maximum reading is attained. In other cases the lag was less than twenty seconds. After the maximum reading was shown, the E.M.F. for several instruments dropped an equivalent of 10° C., during the first ten minutes when sighted as a furnace at 1300° C., while other instruments maintained a constant value. This drop is due to the conduction of heat from the hot to cold junction of the thermo-element, and can be easily minimized by increasing this distance. Preliminary measurements upon the total emissivity of various substances met with in industrial work have shown that the equation

$$\mathbf{E} = b(\log S - \log T)$$

is applicable where $\mathbf{E}$ is the total emissivity, b the exponent for the particular radiation pyrometer used, S the apparent temperature and T the true temperature absolute. Using this relation, $\mathbf{E}$ for iron oxide was found to be 0.86, for nickel oxide 0.83. A slight indication of a temperature coefficient of emissivity was found, $\mathbf{E}$ increasing with temperature, but the variation was almost within the limit of errors of observation.

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THE
PHYSICAL REVIEW.

A POROUS PLUG METHOD FOR THE MECHANICAL EQUIVALENT OF HEAT.

BY J. R. ROEBUCK.

"POROUS plug" is the term applied to experiments like those of Joule and Thompson, where a fluid moves along a tube through a porous obstruction, thereby suffering changes in pressure and in temperature. The initial and final pressures and the initial temperature are usually fixed by the experimenter and the final temperature allowed to adjust itself. In their work as with most of the later workers, the fluid moved along a tube past a thermometer, then through the porous plug, across which therefore there is a drop in pressure, and then past a second thermometer. During the passage through the plug the total energy does not change but it is redistributed. In the case of a liquid the pressure does work against friction in the pores, changing potential (PV) energy into heat, producing when undisturbed a rise in temperature. But the process is usually complicated by a change in temperature due to the change in volume following the change in pressure. When this latter temperature change can be made small and accurately measurable by other means, the change of mechanical energy into heat offers a promising means for the determination of the mechanical equivalent of heat. As compared with Rowland's method it has the advantages of continuous flow experiments where states usually transitory become steady ones and may be investigated at leisure.

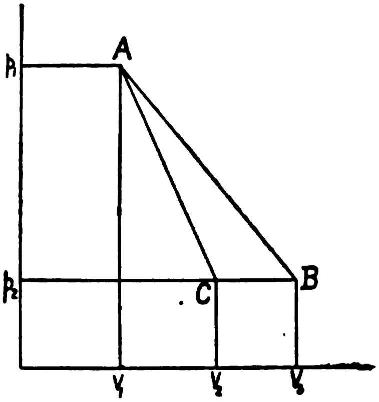
Other observers have noted its advantages, among them Maxwell (Theory of Heat) who gives a mathematical treatment of the case. It has even been tried experimentally but so far as the writer is aware without publication. The unmanageable radiation and conduction losses of the forms of porous plugs hitherto employed would have presented great difficulty. The actual measurements required are limited to the determination of a difference of pressure and a difference of temperature with some definitely determinable corrections which may be made small. The temperature difference across the plug is independent of the rate of flow if there are no heat losses, but depends upon the specific heat of the fluid. A liquid of low specific heat like mercury offers an advantage in the larger temperature difference obtained, but this is offset by the use of water to define the calorie and the accuracy with which the temperature variation of the specific heat of water is known. A liquid is to be preferred to a gas on account of the larger change in PV across the plug due to its small change in volume, which latter also eliminates changes of momentum if the cross sectional areas of flow past the thermometers are similar. Moreover the negative coefficient of expansion of water near the freezing point offers a means of eliminating experimentally the only serious correction. These considerations combined with its cheapness and ready purification lead to the choice of water as the working fluid.

THEORY.

The internal energy of a body is partly kinetic and partly potential, of which only the first part affects the temperature. Change in external pressure on a fluid by affecting the volume will usually cause a shift in the division of energy between the two forms, thus producing a change in the temperature. For the use of the porous plug process as a method of determining the relation between the heat energy produced and the work done upon the fluid, it is necessary to separate this temperature change due to internal energy rearrangements on the relief of pressure, from the temperature change due to the addition of energy in the form of work but which appears in the form of heat. This could be most directly accomplished by carrying out an adiabatic free expansion and a porous plug experiment between the same pressure limits at the same initial temperature. The adiabatic free expansion offers experimental difficulties which have been avoided by the use of a reversible adiabatic expansion. Tamman's (Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen) work on the reversible adiabatic expansion of water has shown that by a suitable choice of initial temperature and initial and final pressures, the final temperature may be made identical with the initial. The employment of these special conditions leads to a marked improvement in the experimental accuracy by limiting the measured temperature change to almost exactly that due to the work done upon the fluid.

In the diagram let the point A represent the initial conditions of pressure, volume, and temperature and the point C the final. Substitute for the actual irreversible porous plug path AC, the reversible path

ABC, where *AB* is a reversible adiabatic expansion and *BC* the addition of heat at constant pressure. Then since the final states are the same,



$$\int_{ABC} du = \int_{AC} du = -\Delta(pv)$$

and

$$\int_{ABC} du = \int_{AB} du$$

$$+ J\int_{B}^{C} C_p dt - p_2(v_2 - v_3).$$

For the reversible adiabatic *AB*

$$\int_{AB} (du + pdv) = 0$$

or

$$\int_{AB} du = -\int_{AB} pdv.$$

Hence

$$-\Delta(pv)_{AC} = -\int_{A}^{B} pdv + J\int_{B}^{C} C_p dt - p_2(v_2 - v_3).$$

But as shown possible by Tamman's work, T_1, p_1 and p_2 are so chosen that *B* is on the same isothermal as *A*, that is T_1. For the particular series of experiments reported here v_2 and v_3 are equal as determined from the data on the coefficient of expansion of water. Computation shows that the term $\int_A^B pdv$ is only about 0.1 per cent. of the term $J\int_B^C C_p dt$ so that

$$\int_{A}^{B} pdv = \tfrac{1}{2}(p_2 + p_1)(v_2 - v_1)$$

may be taken as a sufficiently close approximation especially in view of the small size and constancy of the coefficient of compression. So that calling *C* the mean value in mechanical units between the temperatures T_1 and T_2, we have

$$(p_1v_1 - p_2v_2) = -\tfrac{1}{2}(p_2 + p_1)(v_2 - v_1) + C(T_2 - T_1)$$

or

$$C = \frac{\Delta p(v_1 + v_2)}{2\Delta T},$$

which is the expression used for the reduction of the experimental data. v_1 and v_2 are the specific volumes of the water at p_1T_1 and p_2T_2 respectively, and their values are taken from Landolt's tables. This leaves two quantities to be measured, a difference of temperature and a difference of pressure. Experimentally this required the careful regulation of the initial temperature and the initial pressure. Electrical resistance thermometers were chosen as probably the most accurate means for measuring small differences of temperature and similarly an open tube mercury manometer for the pressure difference. The manageable mercury column limited the pressure difference to about 33 kg/cm^2 and this in turn fixed the temperature difference at about 0.76° C. under the conditions used. The apparatus is described in the following paragraphs.

PUMP.

As the required condition of steady small delivery at high pressure was not found in any commercially made pump, one was designed by the writer for this work and was built by Mr. Foerst, the department mechanician. It is a six plunger-piston pump, with the cylinders all connected in parallel, and all driven from a common crank shaft. The circular spacing of the cranks is in two groups of three each spaced at 120° with a phase difference between the groups of 30°. This phase difference was chosen because the theoretical delivery of three plunger pistons set at 120° gives six maxima and six minima. The second group is thus so set as to give the maxima of delivery coinciding with the minima of the first group. This gives a theoretical delivery varying only 4 per cent. with a frequency of 12 per revolution. In practice the setting of the conical hard rubber valves and the compression of the water in the cylinders probably introduced greater variation than this, though it was smoothed off considerably before reaching the plug by the elasticity of the system of tubes and the inertia of the water. A large Schaffer and Budenberg spring test gauge was connected to the plug chamber and under good working conditions it showed nothing but a barely readable variation per crank shaft cycle. In any case the variations being rapidly cyclic would be integrated similarly by the thermometer and by the manometer. The power was transmitted from the motor by a round belt to a bicycle wheel minus its rubber tire and from there through sprocket wheels and a chain to the crank shaft of the pump. It made a very reliable, cheap, and quiet method of speed reduction.

PRESSURE REGULATOR.

The pressure was controlled by regulating the speed of the D. C. shunt wound motor driving the pump. The apparatus is shown in diagram in Fig. 1. An accurately ground glass-hard steel piston rod stands vertically in a leather-packed stuffing box in a heavy steel cylinder which is connected at its lower end directly to the plug chamber while at the stuffing box end it is filled with castor oil. This piston rod is arranged to rotate without rotating the load of sand and the latter is hung on gimbals to keep it centered. The piston is driven by a round belt from a parallel cylinder thus avoiding any component of the belt tension along its axis. To the load tank are attached 10 loops of high resistance wire connected in series with the armature of the motor. These loops dip into tubes filled with mercury and are supported independently of the tank. If the delivery of the pump was too great the piston rose, throwing resistance into the armature circuit and slowing the motor till the speed fell to the required delivery. While the piston was rising or falling with noticeable speed the pressure rose or fell slightly. Careful tests showed that the pressure was identical whether the piston came to position from above or below. During the readings the conditions were so steady that the piston did not shift more than a centimeter or two an hour and this shift was always a rise due to the slow clogging of the porous plug.

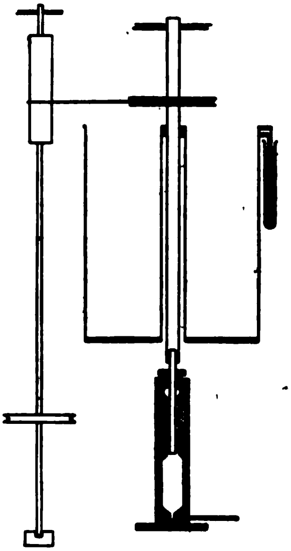


Fig. 1.

Manometer.

A mercury in glass[1] open-tube manometer was built following closely the design of Kammerling Onnes[2] except that water was used to separate the mercury surfaces,[3] and that the cathetometer arrangements were different. The general plan is a set of U-tubes connected in series, the lower halves filled with mercury and the upper with water. The mercury was carefully purified, and distilled water used both here and in the flow work. The difference in level of the mercury surfaces in each of the series of eight U-tubes was read on an invar tape suspended on a track just in front of the tubes. It was kept vertical and straight by a weight, which dipping in oil damped the swinging. The tape was divided accurately into millimeters on the department dividing engine by scratching in wax and etching in acid. This division was compared on a Geneva comparator with the standard invar meter bar just returned from the Bureau of Standards; the correction was small, 13 parts per 100,000 and constant over the tape. For making the readings Professor Mendenhall suggested the use of two mirrors set at 45° to the vertical to avoid the difficulty of getting in line with the mercury surfaces near the ceiling or near the floor. Optical mirrors were required and they were carried on sliding supports on a steel bar set in bearings in the ceiling and floor. The central mirror rotated about a horizontal axis to reflect the image from either the upper or lower mirror into the telescope placed just behind it. All the supports were provided with the necessary motions and carefully adjusted. The base of the pillar was carried on the end of a millimeter micrometer screw provided with gear for adjusting by the operator in a standing position. Readings were made by moving the tape near to the tube, setting the cross hairs on the mercury meniscus, rotating the pillar till the tape replaced the mercury in the field, reading to the nearest millimeter on the tape and the fraction of the millimeter by shifting the pillar with the micrometer screw. The temperature of the mercury columns was determined by five thermometers hung in the manometer case. The large temperature difference between ceiling and floor occurring in a steam-heated room was reduced to about a degree by a fan-driven circulating system carrying the hotter air from the top and delivering it at the bottom of the case.

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[1] Physical Review, 28, 264, 1909.

[2] Proc. Amsterdam Acad., 1, 213, 1898 and 8, 75, 1905.

[3] Cf. Thiesen, Zeit. f. Instrumentkunde, p. 114, 1881.

The manometer was tested by adjusting the levels to balance the pressure due to the loaded regulator, then the load was increased or decreased for a short time and replaced at its old value. The mercury meniscus always returned to its previous position to a part in 10,000 of the total mercury column. The actual pressure given by the regulator was dependent on the temperature of the steel piston and on the hygroscopic condition of the wooden base of the load tank so that it varied from time to time. Where more than one setting was made on the same day, the readings rarely differed by 0.1 per cent.

THERMOSTAT TANK AND PLUG.

The water delivered under steady pressure by the pump was led through 20 meters of copper tubing immersed in a large tank of water, the details of which are shown in Fig. 2. The tank had a separate inner compartment also stirred but containing no heater. The temperature was controlled by a large toluene thermostat provided with a Gowy regulator, which threw a heating current on and off 8 32-c.-p. lamps. The Gowy[1] regulator consists of an excentric for moving the mercury contact maker up and down 1–2 mm. in the thermostat capillary with a period of from 15–30 seconds. The result is that the mercury surface sets itself in the capillary so that the fraction of the period for which the heating current is on the lamps is sufficient to maintain the temperature constant. This eliminates most successfully all the "hunting" of the ordinary thermostat, making it unnecessary for any appreciable quantity of heat to flow into or out of the thermostat bulb. It was found possible to hold the temperature of the plug chamber constant to 2–3 ten-thousandths of a degree for an hour or more. For reasons to be given later it was advantageous to work between 3° C. and 4° C. and to this end the main bath was surrounded by another forming an annular space which was filled with ice and water. This was protected again by a box with sawdust insulation and the temperature could be readily maintained anywhere between 1.5° C. and 5° C.

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[1] Jour. de Physique, 6, 479, 1897.

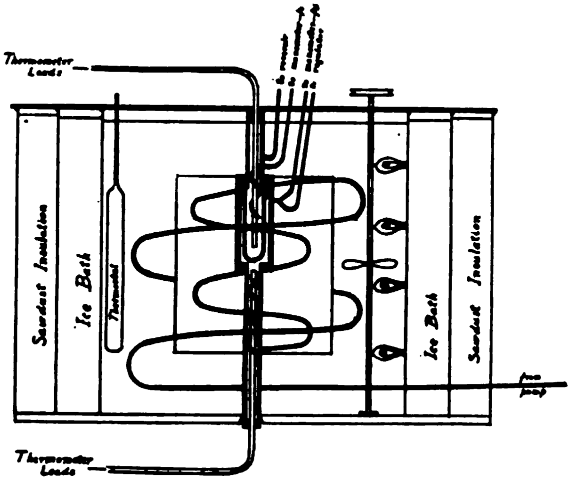

Fig. 2.

Placed axially in the center of the set of tanks was a steel cylinder containing the thermometers and the plug. The water entered this tube from the copper tube at the lower end, passed spirally about the coil part of the platinum thermometer, radially through the plug, spirally about the second thermometer, and on to the reservoir above the pump. From this steel tube small copper tubes led the pressure to the regulator and to the upper and lower sides of the manometer. The arrangements inside the plug are shown in Fig. 3. The plug itself was made of porous porcelain tubing, some with round porous ends and others with flat nonporous ends. The theory of such a porous plug is discussed in an earlier paper by Earl S. Burnett and the author.[1] Since this paper appeared my attention has been called to the fact that Regnault used such a porous plug, which was not known to us at the time. Regnault however says nothing about its protective features but discarded the arrangement and regretted the time put upon it. In the present case the water passes through the plug wall with a rise of temperature. Conduction losses might take place through the walls or through its support. In the former case the heat could only escape to the liquid just entering the wall and hence such conductivity could not be the cause of any continuous heat loss. Radiation might produce a continuous loss if the walls of the plug were at a different temperature from the walls of the container. In cases like this where the temperature gradient is opposed to the flow of the fluid, conductivity outward will be opposed by the flow, and the result will be a slight displacement outward of the temperature distribution. With sufficient flow the rise of temperature of the outer surface will be negligible. This can be rendered still more certain by providing a layer on the outside of the plug nonconducting and sufficiently porous to cause no appreciable pressure drop. This was the more necessary in the present case as the pores of the porcelain filled slowly with a deposit even though pure distilled water was used, and consequently a large part of the pressure drop took place close to the outside of the plug wall. To provide this layer and also to lessen the clogging of the wall, the outside of the plug was always covered with 8 or 10 layers of filter paper and 4 or 5 layers of cotton cloth. That is to say with suitable conditions heat losses through the plug are zero, since the outside surface is at the temperature of the bath. Any effect on the readings of heat losses through the support of the plug was prevented by not allowing the water which passes close to the support to approach the bulb of the thermometer, which was accomplished by dividing the flow as indicated by the arrows in the figure. The effectiveness of the protection from heat losses is proved by the lack of systematic variation of the value of the mechanical equivalent with different rates of flow through the plug.

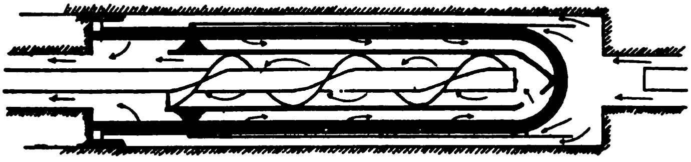

Fig. 3.

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[1] PHYS. REV., 30, 529, 1910.

Early in the work it proved necessary to make the water flow similarly and spirally around the coil of each thermometer. This is probably due to small variations in the temperature at different points in the cross section of the flow, due to the fact that the center of the stream is farthest from the bath water and flows fastest. This was unexpected since stream-line motion breaks down at lesser velocities than those used in the copper tubing. Barnes[1] found the same thing in his work. Arranging the flow spirally mixes it by the swirling motion and gives an average temperature reading. Following the use of this the readings became much more consistent. The spiral was made of a small size rubber tubing held in place by a wire threaded through it and soldered at the ends to the thermometer case. It also made necessary the glass return flow tube inside the plug. The course of the water is shown by the arrows in the figure.

For solutions passing through a porous wall various observers[2] have noted a semipermeable wall effect, that is the dissolved substance is held back somewhat by the wall so that the solution escaping would have a lower concentration than that just at the wall. This mechanically forced dilution of the solution requires work. After a steady state has been reached the fluid passing both thermometers will be alike in concentration of impurities and if the passing of the fluid into and out of the more concentrated zone takes place adiabatically the resultant work required will be zero. In case the distilled water has enough impurities present to show this effect, these changes must have taken place within the filter paper layer where their resultant effect will be zero.

It has long been known that a liquid driven through a capillary in a nonconducting material results in a difference of electrical potential between the ends. In the present case the ends were short circuited by the metal parts so that any motion of charge was not against a difference of potential and hence there was no work involved.

The rate of flow through the plug was measured by reading the pressure drop between the plug and the reservoir by mercury in a U-tube. It was callibrated by reading the pressure drops for a set of rates of flow where these were determined by measuring the delivery in a definite time. No attempt was made to read the flow to better than 1 per cent. accuracy.

THERMOMETER RESISTANCE BOX.

The resistance box was of the regular equal-arm Wheatstone bridge type, with solder or mercury connections in heavy copper throughout.

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[1] Phil. Trans. Roy. Soc., *A*, 199, 149, 1902.

[2] Cf. Bigelow and Bartell, J. Am. Chem. Soc., 31, 1194, 1909.

The coils of manganin or advance wire, silk-covered, were wound noninductively on metal spools, heavily shellacked, and held at steam temperature for days for annealing and drying. The unit of resistance was approximately ¼ ohm. One centimeter of bridge wire corresponded to 0.002 units. The ratio coils were wound noninductively and together on the same spindle, with the four terminals dipping in four mercury cups so that by lifting and rotating through a right angle the ratio coils could be reversed. Their ratio differed from unity by 1 part in 30,000 throughout the work. A mercury cup commutator was used for making the thermometer connections. A removable coil with terminals in mercury cups served to balance most of the resistance of the thermometer. Its place could be taken by a series of coils approximately equal to the box coils, whose use greatly facilitated the box callibrations. Reference must be made to Barnes's paper cited above for the general method of callibration of coils and wire. The box was provided with heating coil, stirrer, and thermostat, and the temperature held at 25° C. during use.

Box Coil Calibrations.

Date.	Nov. 23, 1910.	Dec. 15, 1910.	Feb. 21, 1911.	Mar. 13, 1911.	Sept. 9, 1911.	Nov. 7, 1911.	Feb. 6, 1912.
Coil.	1	2	3	4	5	6	7
0.0625	−0.7	−0.5	−0.2	−0.7	−0.3	−0.2	−0.8
0.125	−1.6	−1.7	−2.5	−1.7	−2.0	−1.5	−0.9
0.25	−4.8	−4.2	−3.9	−4.6	−5.3	−3.2	−3.5
0.5	1.1	0.9	0.5	1.2	−0.2	1.7	1.9
1.0	0.3	0.3	1.0	0.3	1.5	2.4	2.2
2.0	−2.6	−2.2	−2.4	−2.8	5.7	0.9	1.9
4.0	−3.7	−3.6	−3.7	−3.9	10.0	2.7	3.1
8.0	−3.0	−6.8	−7.0	−9.0	16.7	3.4	−1.1
16	−0.2	0.4	−3.9	−1.7	8.2	1.2	28.8
32	37.1	42.4	36.6	38.1	36.3	49.8	28.0
64	0.0	0.0	0.0	0.0	0.0	0.0	0.0

The corrections are box units × 10^4.

The box was callibrated at frequent intervals and it quickly developed that the resistances were changing continuously by quite serious amounts. Rosa[1] attributes this to the varying hygroscopic condition of the shellac resulting in variation in strain on the wire. As he recommends, the coils were enclosed in moisture tight containers which reduced but did not eliminate the variations. Addition of scrap metallic calcium to the bath oil as a water and acid absorbing agent did not help materially nor did omitting the shellac on some test coils. The variations now however were of quite manageable size entering only into the actual temperature readings and hardly at all into the differential readings used in the work. The callibrations covering the period of the readings are given in Table I. where the numbers are the corrections in box units times 10^4.

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[1] Bull. Bur. Stand., 5, 553, 1907.

The galvanometer was of the Broca type with all copper circuit and magnetic shielding. It was used only as a zero instrument. The sensibility was about 10^{-10} and was kept sufficiently high to allow of setting with certainty to 0.0001° C. In both callibration and use a current of about 0.01 ampere was kept flowing continuously, and readings were made by reversing the current which therefore did not vary the slight heating effect and also doubled the galvanometer reading.

THERMOMETERS.

To approach the desired accuracy in the temperature readings it was necessary to read to 0.0001° C. This made imperative the use of high resistance in the thermometers and all those used in the readings had fundamental intervals of about 25 ohms. Even with fine wire the standard mica frame became too bulky for the purpose; the most satisfactory one found and that used with the platinum thermometers, was made by cutting a double thread on a soapstone cylinder and hardening it by heating to a white heat. It was then wound so that the wire fell below the edge of the thread. The four leads were threaded into the end of the cylinder, thus supporting it, while the thermometer wire was led out through small holes and silver soldered to the heavy platinum leads. These in turn were silver soldered to the copper wire which was carried out of the brass case through a hard rubber block made tight by marine glue. Everything was repeatedly tested for insulation which was made perfect before use. The case was provided with an opening to the air through a calcium chloride tube and everything was put together dry. The platinum wire was obtained from the Cambridge Scientific Instrument Co., 5 meters of 0.1 mm. wire being used in each thermometer. They were annealed at a low red heat and callibrated at 0° C., 100° C. and 444.6° C. The ice point determinations were made in a double ice bath protected by an air space and asbestos covering. Barnes has shown, and my experience agrees with his, that the temperature of the ice bath is very distinctly a function of the rate of melting. This melting point bath was arranged for a forced circulation down through the inner central cylinder and up the outer. In case the stirring was stopped the temperature always fell a small amount. The ice in the inner compartment melted very slowly so that it appeared advisable to break the ice fine and use the inner tank unstirred except for shifting the thermometers which produced usually a slight rise in the temperature followed by a fall close to the former value. The steam point was determined in the usual well protected steam bath. The pressure was read on an accurate Fortin barometer. Three groups of fundamental intervals for different thermometers are given to show the concordance obtained.

100.695	104.062	106.602
100.711	104.073	106.568
100.696	104.072	
100.706		

The complete data for the thermometers as used for the data reported farther on, is given in the following table.

THERMOMETER DATA.

	A	*B*
Resistance at 0° C.	295.93	294.09
Resistance at 100° C.	399.88	398.16
Fundamental interval	103.95	104.07
Resistance at 442.9° C.	432.90	436.07
Delta	1.748	1.567
$\frac{R_{100} - R_0}{100\ R_0}$	0.0035127	0.0035387

The sulphur point was taken as 444.6° C. The numbers are in box units, approximately ¼ ohm. The platinum used was part of a sample studied by the committee of the British Association and later taken over by the Cambridge Scientific Instrument Co. They report the delta as 1.62. The difficulty over the zero variation referred to below, led to the rewinding of the wire several times, which will probably account for the difference between the two thermometers and also for the variation in the deltas.

In work with these small temperature differences the greatest source of uncertainty of the platinum thermometers arose through the persistent and erratic shifts of zero resistance. Since the resistance was being read to less than a part in a million it was not surprising. In no case did the resistance return to the former ice point value after being at the steam temperature. That it was not due to the box coils is shown by the variation of the difference in resistance of the two thermometers both in the ice bath and in the thermostat bath. It was often of the order of thousandths of a degree. As discovered later, part but not all, was due to defective leads which changed their relative resistance when moved about, but the variations were also noted when the leads were not disturbed. It introduced a quite uncontrollable factor into the temperature readings and was undoubtedly the cause of some of the error in the mechanical equivalent determinations.

In an effort to run down the trouble, thermometers were made of fine iron wire, silk covered, and wound on thin iron cylinders as suggested by Barnes's work with his microthermometers. Their zeros were decidedly more constant but much the same erratic variation occurred in the values of the mechanical equivalent as determined with them. These results supported the belief that the platinum thermometers were much more reliable than had been inferred from the mechanical equivalent results. Further confirmation came from the excellent agreement between the calculated and determined differential readings at a series of temperatures near 4° C.

WORKING TEMPERATURE.

In the theoretical discussion above, reference is made to the possibility of having a zero change of temperature on reversible adiabatic expansion between given pressure limits by a suitable choice of initial temperature. An experimental study soon to be published showed for the pressure limits 34 kg/cm^2 to 1 kg/cm^2, that the temperature was 3.59° C. Between the limits 3.53° C. and 3.65° C. the temperature change was less than 0.0001° C. and hence all of the readings were made with bath temperature lying between these limits. The similar pressure limits were 31.5 kg/cm^2 and 35.5 kg/cm^2.

EXPERIMENTAL METHOD.

The bath and the resistance box were first brought to the desired temperatures and the thermostats set working steadily. The two thermometers were placed for their full case lengths in the water of the bath with the bulb end in the inner bath and their difference of resistance read with a steady current till the readings became constant for 5 to 10 minutes. They were then put into their places in the system with as little exposure to room temperature as possible and the pump started. Throwing this sudden change of load on the thermostat upset its steady working for a few minutes but as soon as the pump and the supply tank were cooled down somewhat and reached a steady state the thermostat was back in steady working order. The speed of the pump was adjusted to give nearly the flow required after which the regulator held the pressure constant while the flow decreased somewhat due to the partial clogging of the plug by fine suspended material in the water. This clogging decreased rapidly as the water cleared of suspended particles. The pressure was then admitted very slowly to the manometer. If the water surfaces were displaced rapidly by the mercury, the water clung in a thick layer to the glass in the capillary tubes and when the flow had ceased, the water gathered together, making small gaps in the mercury columns, which consequently had to be carefully guarded against. At the same time the pressure was applied, the air circulating fan was started. The compression of the mercury and of the water, the expansion of the glass, and the admission of cold water from the circulating system, all tended to disturb the temperature conditions so that the manometer was never read till at least half an hour after the pressure was first applied. During this time the plug conditions and the thermostat were becoming steady. As soon after this as the plug temperature difference became constant for 5–10 minutes and the manometer surfaces showed no shift for the same time, the valve to the manometer was shut down, the pump stopped, and the reading of the manometer differences of level carried out as rapidly as possible. The readings were made from the low pressure surfaces to the high pressure surfaces of the eight tubes, reading the temperature on the five case thermometers during the process, and the setting on the first tube was repeated. It sometimes showed a rise and sometimes a fall of the higher surface, never more than a millimeter either way, and was as small as could be expected considering the way the tape was carried on the sliding support and also considering the way the temperature of the water and the mercury could have varied. The manometer did not leak as shown by leaving the pressure on it for hours or a small pressure for days. At the completion of the manometer settings requiring about 25 minutes, in the later readings when experience had shown it to be advisable, the thermometers were replaced in the inner bath and the difference of their resistances again determined. In the earlier readings with the platinum thermometers this difference in their resistances was determined before or after the plug reading, and differed so markedly from day to day that a part of the variation of the results is to be attributed to this cause.

In the only group of readings considered of sufficient accuracy to report in detail the procedure was varied somewhat to avoid the necessity of comparing the thermometers at the bath temperature. A determination of the flow difference of temperature was made and the manometer read, the thermometers were then reversed in position and both readings repeated. The mechanical equivalent (C) calculated from the sum of these differences of temperature and differences of pressure eliminated the determination of the difference of resistance at the same temperature and all that was required of this difference of resistance was that it should remain constant during the pair of readings. The complete set made in this way is reported.

No.	Press. Change.	Temp. Change.	Temp.	Flow.	C	Per Cent.
1	65,808	1.5281	3.556	675	4.2081	−0.04
2	65,446	1.5187	3.570	1,425	4.2123	+0.06
3	65,572	1.5230	3.550	1,175	4.2086	−0.03
4	65,706	1.5272	3.551	1,080	4.2057	−0.10
5	65,669	1.5259	3.550	1,025	4.2069	−0.07
6	65,683	1.5279	3.550	980	4.2027	−0.17
7	65,812	1.5295	3.537	770	4.2065	−0.08
8	65,867	1.5313	3.537	650	4.2051	−0.12
9	65,871	1.5290	3.533	400	4.2127	+0.04
10	65,559	1.5196	3.571	1,240	4.2156	+0.17
11	65,460	1.5193	3.557	1,370	4.2116	+0.05
12	65,464	1.5156	3.557	1,370	4.2221	+0.29
				Average	4.2099	

In the above the pressure is expressed in kg/cm^2, the temperature in degrees centigrade, the flow in c.c./min., and C in joules/calorie in terms of the calorie at the average temperature 3.99° C. In the calculations of these readings the density of the water and of the mercury at the average temperature is taken from the tables of Landolt-Bornstein, as is also the specific volume of the water and the coefficients of compressibility. The small correction for the error of the tape was applied, but no correction for the temperature since the coefficient of expansion is so small. The value of gravity used, 980.36 cm/sec^2 was that determined by E. Smith.[1]

In the above table all the readings except the last (No. 12) were made with the same plug having a round porous end, but the flow arrangements differed slightly at different times, since it was necessary to dismount the plug to clean it and the flow guides could not be replaced in identically the same way. The rate of flow varies markedly but the value of the mechanical equivalent shows no systematic variation with it. This proves the above theory of this form of porous plug at least to the accuracy here shown. It also shows that water takes a very short time to attain its equilibrium condition after the removal of pressure which was not by any means to be confidently expected. The average of the whole set unweighted is 4.2099. The last reading was made with a plug with a metal (non-porous) end and although it was well covered there was undoubtedly some heat loss and the value of C would be too high. If this is omitted the average becomes 4.2087, while Barnes's value for this temperature is 4.2078. Barnes's method is so different from the present one, that this agreement (0. 02 per cent.) gives ground for the belief that systematic errors are fairly well eliminated and that those remaining are largely chance errors of individual readings which will average out more or less completely. On account of the unusual working temperature direct comparison with other worker's data does not seem profitable at this time.

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[1] U. S. Coast and Geodetic Survey, Special Publication No. 12, page 9.

The probable sources of uncertainty are of some interest. The regulation of both temperature and pressure left nothing to be desired. The most serious known source lay in the uncertain variation of the differential resistance of the platinum thermometers. All the experimental evidence indicates that the manometer recorded pressure to the desired accuracy, and the only further confirmation would be to test its reproducibility by means of some reliable constant pressure. The change produced by placing the flow guides around the thermometers leaves some doubt as to whether error due to irregularity of flow has been absolutely eliminated. It is the writer's belief that the data presented in this paper, while the result of several years work, is not yet as consistent as the method can be made to yield; and it is his intention to return to the work again as soon as circumstances allow.

My thanks are due to Professor Snow and to Professor Mendenhall for placing the laboratory facilities at my disposal for the work, and to Professor Mendenhall also for his very valuable criticism of the manuscript.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WISCONSIN,
January, 1913.

A STUDY OF SOME CHANGES IN THE AIR-LIQUID CONTACT POTENTIAL DIFFERENCE.

By G. W. Moffitt.

IN spite of the fact that much work has been done on the investigation of contact potential differences very little can yet be said with certainty, except in the case of metals, concerning either the nature or the magnitudes of the potential differences between different substances in contact. The early investigators were handicapped by apparatus of low sensitiveness and in some cases by a preconceived and decided notion of the phenomenon under investigation. In fact, the history of the subject presents to us a long series of lengthy wordy arguments between the exponents of the electrochemical theory and those of the contact theory. Often there is little experimental foundation for the conclusions reached, direct experimental results being discordant seemingly from the very nature of the phenomenon. And yet we find instances where results are given to the fourth decimal place when the apparatus was inaccurate in the third place and the observed quantity varied in the second place.

The greater part of the time and thought of investigators in contact electricity has been directed toward the solution of the problem for metals. Nevertheless we find at an early date a few investigators who did very good work in pioneering the difficult problem of metal-liquid and liquid-liquid contact potential differences. We find that Volta, Davy, Buff, Becquerel, Pfaff, Péclet, Kohlrausch, Hankel, Gerland, Clifton, Ayrton and Perry, and others have made experiments using various inductive methods.

As early as 1807 Davy,[1] in a paper entitled "Some Chemical Effects of Electricity," describes some condenser experiments which he had made using various liquids.

In 1824 Becquerel[2] attempted the investigation of metal-liquid contact potential differences. He placed the liquid in a metal vessel which stood on the upper plate of a condenser connected to an electroscope, and connected the liquid to the condenser with his fingers. He tried merely to find the sign of the electrification.

[1] Ann. de Chim. [I.], LXIII., p. 230, 1807.

[2] Ann. de Chim. et de Phys., XXV., p. 405, 1824.

Buff[1] made the lower plate of his condenser of the metal to be examined. Above it he placed a sheet of glass and on the glass a piece of filter paper soaked in the liquid. He connected the moist filter paper to the metal plate by means of a wire of the same metal.

Kohlrausch[2] made some experiments on the difference of potential of liquids in contact. He too used filter paper wet with the liquids as his condenser plates. For this reason, as we shall see later, we cannot give much weight to his results.

Hankel[3] used a modified Kohlrausch method and investigated metal-liquid potential differences without introducting blotting paper, fingers, or glass, as the earlier experimenters had done. He employed a wide funnel connected by a tube to a small cup. The vessel was filled level full of the liquid and the metal electrode was placed in the cup. Immediately above the liquid in the funnel was a copper plate. This plate was put in metallic contact with the electrode, then insulated, lifted, and connected to a Hankel electrometer. A zinc plate was then substituted for the liquid and the experiment was repeated. The metal-liquid potential difference was then deduced in terms of the contact potential difference between zinc and copper. Air-liquid contacts were neglected throughout the work. The observed values were found to vary considerably; for instance, freshly polished copper and water gave values from 0.09 to − 0.11 Zn/Cu.

Clifton[4] used a quadrant electrometer, one pair of quadrants connected to the upper condenser plate, the other pair to the lower plate. The upper plate was of the metal under observation. On the lower plate was placed a dish of the liquid to be used and an electrode of the same metal as the upper plate dipped into the liquid and made metallic contact with the lower plate. A means of charging the quadrants and the connected condenser to any desired potential difference was supplied through a key which could also serve to bring the quadrants to the same potential.

He assumed that the surface condition of his condenser plate was a constant and made no mention of the possible existence of a potential difference at the air-liquid contact. His results are referred to Zn/Cu, which he seemed to think was more constant than a Daniell or a Clark cell. He gave it as 0.8516 volt, but it is to be noticed that separate determinations disagreed in the second decimal place. He also gives potential diagrams of various voltaic circuits. These diagrams are apt to prove misleading, however, because the magnitudes of the different potential differences in the circuit, to say nothing of their signs, are as yet wholly undetermined.

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[1] Ann. d. Chem. u. Pharm., XLII., p. 5, 1842; XLV., p. 137, 1844.

[2] Pogg. Ann., LXXVI., p. 200, 1850.

[3] Pogg. Ann., CXXVI., p. 286.

[4] Proc. Roy. Soc., XXVI., p. 299, 1877.

A most thorough and comprehensive investigation of contact potential differences with liquids was begun in 1876 by Ayrton[1] and Perry in Japan. They devised an ingenious method but the apparatus required was ponderous and cumbersome. With it they made a great many determinations of metal-metal, metal-liquid, and liquid-liquid potential differences. The principle of their method was as follows:

"Let 3 and 4 be two insulated gilt brass plates connected with the electrodes of a delicate quadrant electrometer. Let 1 under 3 and 2 under 4 be the surfaces whose contact potential is to be measured. 3 and 4 are first connected together and then insulated, but remain connected to their respective electrometer quadrants. Now 1 and 2 are made to change places with one another, 1 being now under 4 and 2 under 3, then the deflection of the electrometer will give a measure of the difference of potential between 1 and 2."

The experimental difficulties encountered in interchanging 1 and 2 and still preserving the necessary constant capacity relations, especially when one or both surfaces were liquids, will be at once realized.

In their measurements no account is taken of air-metal contacts, and air-liquid contacts were considered negligible, if they had any influence at all. Before they finished their work, however, their views underwent a change and in their last paper they clearly state that their experiments leave the question of air-liquid contacts undecided. If 1 and 2 were two liquids, L_1 and L_2, what they really measured was

$$L_1L_2 + L_2\,\text{air} - L_1\,\text{air},$$

that is, the liquid-liquid contact potential difference plus the difference of the two air-liquid contact potential differences. They placed great confidence in the constancy of the contact potential difference between zinc and copper which they used as a standard at 0.75 volt (Clifton gave it as 0.8516 volt). And they agreed with Clifton that it was more constant than a Daniell or a Clark cell, although Pellat found it to vary as much as three tenths of a volt. They have tabulated the results of numerous observations which on examination reveal discrepancies many times larger than the limit of sensibility of their apparatus.

Turning to electrochemistry we have the solution pressure theory of electrode potentials and of diffusion potential differences developed by Nernst, Ostwald and others. For dilute solutions of electrode salts theory agrees fairly well with experimental results on concentration cells.

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[1] Phil. Trans., Part I., 1880.

For measurements of single potential differences the electrochemists depend on the Lippmann electrometer and the dropping mercury electrode, which are based on the Helmholtz theory of the electric double layer. These are familiar to most physicists and it is not the writer's intention to review the numerous researches in this field of electrochemistry. There are, however, a few papers that may well be noticed here. Billitzer[1] has shown that the maximum surface tension for mercury in contact with a liquid does not necessarily occur when there is no difference of potential between the metal and the liquid. He showed by several methods that it may vary as much as several tenths of a volt, and he came to the conclusion that methods of measuring metal-liquid contact potential differences depending on the Helmholtz theory of the electric double layer are inaccurate. Krouchkoll[2] found similar results with wires under tension as electrodes. These results were also confirmed by Exner and Tuma, and also by Brown.[3]

Summing it all up, we may say that no experimental determination that is entirely free from objection has as yet been made of any electrode potential, or of any liquid-liquid potential difference, and that the question of the air-liquid contact potential difference has merely been raised.

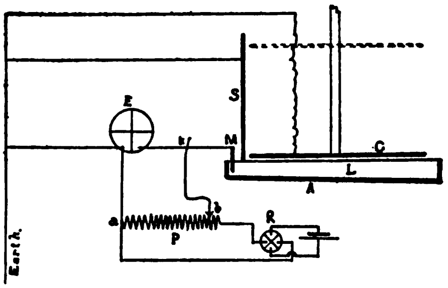

Fig. 1.

The purpose of this investigation was to devise a simple and satisfactory method for the study of contact differences of potential in those cases where liquids enter into consideration, and to seek out and eliminate if possible the unknown sources of erratic error which have caused such discrepancy in the experimental results of previous investigators. As is usually the case, the whole aim of the work has not been realized, but enough has been done to show that the problem of contact potential differences with liquids is more complex than has been thought. Factors heretofore neglected will be shown to play an important part, at least at the air-liquid contact.

A form of the compensation method was used. Fig. 1 is a diagram of the electrical connections. *A* is an insulated glass vessel 24 centimeters in diameter and less than a centimeter in depth, in which is placed the liquid (*L*) under observation. *C* is a lacquered brass plate 20 centimeters in diameter, which, in its lowest position, stands a few millimeters above the surface of the liquid. It is arranged so that it may be easily raised to a height of 6 or 8 centimeters above the liquid while the observer is watching the electrometer scale. This plate is connected permanently to earth. *M* is a small electrode of the metal under observation. It is supported on an insulating stand entirely separate from the glass vessel and it is connected permanently, during an experiment, to he insulated quadrants of a Dolazalek electrometer, by means of a mercury cup and a brass wire. The other pair of quadrants is permanently connected to earth. *S* is an earthed electrode screen that prevents any inductive effect on the electrode by the motion of the plate *C*. *P* is a Wolff potentiometer by means of which the insulated quadrants and the electrode are brought to any desired potential through the key *k*, which also serves as the earthing key. *R* is a reversing key in the main circuit of the potentiometer which permits either positive or negative potential to be applied to the electrode. The entire apparatus, except the main potentiometer circuit and the galvanometer, is protected by earthed screens.

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[1] Zeitschr. Electrochem., 14, p. 624, 1908.

[2] Ann. chem. phys. [VI.], 17, p. 129, 1889.

[3] Phil. Mag. [V.], 17, p. 384, 1889.

In some of the later experiments metal cell vessels were used instead of the glass vessel. One of these was plated with tin, the other with copper, so that various solutions might be used without chemical action on the containing vessel. When the metal vessels were used they were not filled level full, as was the glass vessel, and to prevent error due to induction between the condenser plate and the vessel rim a cylindrical guard ring of lacquered brass was used as shown in Fig. 2. This guard ring was also used in place of the electrode screen in the later experiments using the glass vessel.

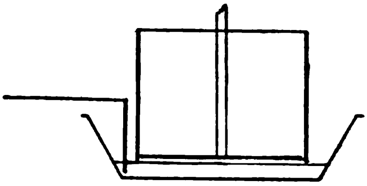

Fig. 2.

In making a reading the vessel was carefully cleaned, placed in position, and filled with the liquid to be investigated. The electrode was then rubbed bright with sandpaper, cleaned with dry filter paper, and placed in position. The condenser plate was placed at the bottom of its range of motion, and a little time allowed for the electrode potential to become steady. The potentiometer circuit was closed and the dials adjusted to any desired potential drop along *ab*. Then the key *k* was opened. On raising the plate *C* there was, in general, a rush of electricity to or from the electrometer. But if the *surface* of the plate and the *surface* of the liquid were at the same potential no redistribution of charge would take place and no *change* of the electrometer reading would be observed. The potentiometer reading would be the value sought. The electrode was then removed, wiped with clean filter paper, replaced, and after a short time, the reading was checked.

It will be seen that all the advantages of a null method are retained, the electrometer acting merely as an indicator. The sensitiveness of the apparatus depends not only upon the electrometer, but also upon the ratio of the electrometer capacity to the cell capacity, and with the apparatus used it was possible to determine the balanced point within 0.002 volt. This was sufficiently sensitive for the work.

Before readings of any value could be made it was necessary to obtain a plate C whose surface potential would remain nearly constant. Pfaff and others have found that for dry or moist air and other gases, the surface potential of lacquered plates is not affected as long as there is no visible chemical action. Although used a few millimeters above the surface of liquids the plate gave no trouble. During eleven days the observed values for a copper electrode in glycerine did not vary by 0.01 volt. Copper-glycerine was occasionally used as a check on the constancy of the plate surface.

From Fig. 1 it is easily seen that what is experimentally determined is

$$K + aL + LM = E, \tag{1}$$

where K is the constant potential difference between the plate and the air, aL the potential difference between the air and the liquid, and LM that between the liquid and the electrode. If two liquids be used in succession with the same electrode we have

$$K + aL_1 + L_1M = E_1, \tag{2}$$

$$K + aL_2 + L_2M = E_2. \tag{3}$$

If a diffusion cell be set up using the two liquids we measure

$$ML_1 + L_1L_2 + L_2M = V. \tag{4}$$

Combining these three equations we have

$$L_1L_2 + L_2a - L_1a = V + E_1 - E_2. \tag{5}$$

This is in fact, what Ayrton and Perry measured, considering L_2a and L_1a negligible. With their apparatus air-liquid contacts could not be studied separately.

Consider again the observation equation

$$K + aL + LM = E.$$

The value of K may by reason of occasionally repeated check determinations, be assumed constant, although we have no means of knowing its actual magnitude. For a given liquid it is hardly possible that LM varies from time to time, and at any rate it is subject to experimental determination. We are in a position to find out whether La is a variable depending on surface condition of the liquid, gas content, and so on, and thus show its existence. And since the influence of the negative radical on the electrode potential is known to be small by reason of electrochemical data, LM will not vary much for different electrode salts. The influence of the negative radical on the air-liquid contact may then be studied.

A number of solutions of copper sulphate of different concentrations were made up. A copper electrode was used and E determined for the different concentrations. The results are plotted in Fig. 3, Curve I. This curve shows the variation of $aL + LM$ with concentration of the solution, but it does not give actual values since all readings are affected by the constant K. The same solutions were used two weeks later and Curve II. shows the results. Later on fresh solutions were made up and used with the results shown by Curve III. With zinc and zinc sulphate solutions the results were even more erratic as is shown by Curves IV. and V., which are for two sets of solutions.

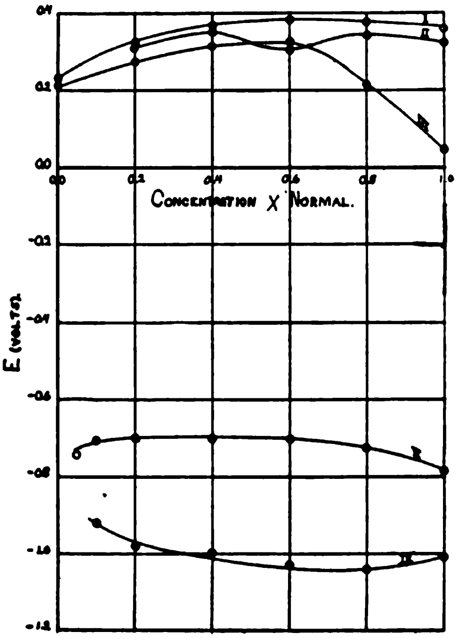

Fig. 3.

As long as results vary in this erratic way it is useless to measure the E.M.F. of the various concentration cells needed to compute $L_1L_2 + L_2a - L_1a$ for different concentrations of the same solution, and to tabulate results.

If these erratic values were due to a change in the value of K from day to day the result would be to add a constant to all the observed values, and the form of the curve would not be changed. Irregular variations of K large enough and rapid enough to account for the discrepancies seem very improbable. It is also improbable that LM can differ much for two solutions of the same salt at the same concentration. Neither is it conceivable how *LM* for the same solution could change so much in a few days when the solution was kept in a clean glass-stoppered flask. The most probable place for differences to occur seemed to be at the air-liquid contact, and experiments were then performed to determine this point.

It was thought that the gas content of the solution might affect the air-liquid contact potential difference and with this in mind the following experiments were performed. The time of observation is recorded merely to show that the readings were made rapidly enough to eliminate the possibility of any disturbing variation of *K*. The experiments given are only a few of those performed with the same general results.

Copper Electrode. Normal Sodium Chloride Solution. Tinned Cell Vessel without Guard-Ring.

Liquid Surface Condition.	*E* (Volts).	Time.
Solution placed in cell	−0.01	3:45
Air bubbled into the solution	−0.11	4:00
Solution poured into beaker and at once poured into cell	−0.02+	4:18
	−0.03	4:30
Air bubbled in place	−0.13	4:35
	−0.13	4:50
Air bubbled again	−0.14	5:00
Poured into beaker and at once returned to cell	−0.04	5:10
Air bubbled in place	−0.12	5:15

Copper Electrode. Normal Sodium Chloride Solution. Tinned Cell Vessel with Guard-Ring.

Liquid Surface Condition.	*E* (Volts).	Time.
Solution placed in cell	−0.11	9:00
Air bubbled in place	−0.16+	9:10
Air bubbled again	−0.17	9:20
Poured into beaker. At once returned to cell	−0.05+	9:30
Air bubbled in place	−0.16	9:45
Swept with clean filter	−0.23	9:50
Poured into beaker and at once returned to cell	−0.09	10:00
Swept with clean filter	−0.24	10:10

From the first experiment it is evident that the variation in the air-liquid contact potential difference is not wholly due to dissolved gases since pouring the solution out of the cell and at once returning it returns the reading to its first value. The change due to air bubbling is practically the same in each case, and causes a shift toward negative values. In the second experiment the guard-ring was used and actual values are different, but the same general effect due to pouring and to air bubbling is noticed. Sweeping with filter paper produces an effect much greater than that produced by air bubbling and in the same direction.

In the following trial with a 0.4 normal copper sulphate solution in the copper-plated vessel using a copper electrode, the liquid surface was repeatedly swept until a steady value was obtained.

Liquid Surface Condition.	E (Volts).	Time.
Solution placed in cell	+0.31−	1:55
Swept with clean filter	+0.21	2:00
Poured into beaker and at once returned to cell	+0.27	2:07
Swept with filter paper	+0.17−	2:13
Air bubbled in place	+0.13	2:25
Swept with clean filter	+0.06	2:30
Air bubbled in place	+0.06	2:40
Swept with clean filter	+0.03	2:43
Again swept with filter	+0.01	2:46
Again swept with filter	−0.00+	2:50
Again swept with filter	−0.02	2:55
Again swept with filter	−0.03−	3:00
Poured into beaker and at once returned to cell	+0.11	3:06
Again poured into beaker and returned to cell	+0.20	3:15
Again poured into beaker and returned to cell	+0.22	3:25
Again poured into beaker and returned to cell	+0.24	3:30
Drop of kerosene on surface	0.00	3:37
Another drop added	−0.02−	3:41
Poured into beaker, vessel cleaned, solution returned	+0.02	4:25
A drop of kerosene added	−0.02	4:30
About 1 c.c. kerosene added	−0.01	4:35

It is seen that a limiting low value was approached as the surface was repeatedly swept with filter paper. It is also of interest to note that a few drops of kerosene instantly produced the same effect as did continued sweeping with filter paper, and the addition of considerable kerosene produced the same change as did a very thin film of it.

The effect of drawing a clean glass rod reaching clear across the vessel, over the surface thus securing a clean surface, was then tried. In order to do this the glass vessel was used level full of the liquid. The copper electrode and the 0.4 normal copper sulphate solution was used with the following results.

Liquid Surface Condition.	E (Volts).	Time.
Poured into vessel	+0.17−	10:00
Swept with clean filter	+0.12	10:08
Again swept with filter	+0.10	10:11
Swept with clean glass rod	+0.29	10:20
Swept with filter paper	+0.21−	10:30
Swept with clean glass rod	+0.36	10:36
Again swept with rod	+0.39	10:44
Again swept with rod	+0.42	10:49
Again swept with rod	+0.43	10:52
Again swept with rod	+0.43+	10:55
Swept with clean filter	+0.29	11:00
Again swept with filter	+0.19	11:02
Again swept with filter	+0.14	11:06
Small drop kerosene added	+0.10	11:08
Another drop kerosene added	+0.09	11:12
Swept with clean glass rod	+0.14	11:16

In every case sweeping with the glass rod raised the value toward a maximum limit, and continued sweeping with filter paper reduced the value toward a lower limit.

A normal sodium chloride solution was next tried with the copper electrode, and the effects of alcohol and ether vapor and kerosene are shown below.

Liquid Surface Condition.	E (Volts).	Time.
Swept several times with glass rod	+0.05	9:15
Again swept with glass rod	+0.06	9:22
Undisturbed	+0.06−	9:36
Three drops alcohol put on. Negative at first but before a reading could be made was	+0.03	9:44
Three more drops alcohol, first reading	0.00	9:49
	0.00	10:12
Ether vapor poured on	−0.10	10:15
Undisturbed	−0.03	10:28
Undisturbed	−0.05	10:39
Drop kerosene put on	−0.18	10:46
Another drop kerosene put on	−0.21+	10:50
Another drop kerosene put on	−0.22	10:52
Another drop kerosene put on	−0.22−	10:55

Besides showing the effects produced by various substances this experiment shows three separate determinations with distilled water agreeing well among themselves. In all the cases tried the difference between the high clean surface value and the low filter swept or kerosene surface was found to be about 0.3 volt.

Copper Electrode with Distilled Water using Glass Vessel with Electrode Screen.

Liquid Surface Condition.	*E* (Volts).	Time.
Swept several times with glass rod	+0.29	9:30
Again swept with rod	+0.29	9:34
Again swept with rod	+0.29 −	9:36
Screen replaced by guard ring	+0.29	9:48
Vessel emptied. Refilled. Swept with glass rod	+0.28	9:55
Swept some more with rod	+0.27 +	
Some cork dust sprinkled on	+0.26	10:00
Drop of kerosene. Cork dust swept to edge of vessel	+0.01	10:06
Another drop of kerosene	−0.03 −	10:10
Another drop of kerosene	−0.03 −	
Cell emptied, cleaned and refilled. Swept with rod	+0.28 +	10:24
Drop toluene added. A decrease but before a reading could be made it was	+0.27	10:39
More toluene added	+0.25	10:42
Drop cotton-seed oil added	+0.04	10:55
Several drops more	+0.04	10:57
Drop of kerosene added	+0.04 +	10:59
Several drops more	+0.03 −	11:02
Cell emptied. Refilled without cleaning. Some oil still on the surface	+0.03	11:20
Swept[1] several times with rod	0.00	11:30
Swept[1] several times with rod	−0.04	11:35
Swept[1] several times with rod	−0.05	11:41

Since the air-liquid contact potential difference has thus been varied as much as three tenths of a volt its general existence cannot be denied. In what special cases it may be zero or negligibly small we do not know Neither do we know its magnitude nor its sign in any case, but we see from the above experiments that the clean liquid surfaces used are more positive to air than are the contaminated surfaces.

Experiments were next made to find the variation of *E* with the concentration of the solution, taking in each determination the final value for a clean liquid surface. The copper electrode was used in all these experiments.

NaCl (Normal Solution).

Swept with glass rod	−0.05
Swept some more	−0.02
Swept some more	0.00
Swept some more	+0.01 −
Swept some more	+0.01 −

NaCl (0.4 Normal).

Swept as before	−0.03
Swept some more	+0.05
Swept some more	+0.04
Swept some more	+0.05

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[1] The sweeping removed the small globules of cottonseed oil leaving a film of kerosene.

NaCl (0.2 Normal).

Swept as before	+0.08
Swept some more	+0.11 −
Swept some more	+0.10 −
Swept some more	+0.10
Swept some more	+0.10

Water (Distilled).

Swept as before	+0.28
Swept some more	+0.28

This gives clean liquid values for *E* as follows:

Water	+0.28
NaCl (0.2 normal)	+0.10
NaCl (0.4 normal)	+0.05
NaCl (normal)	+0.01 −

Solutions of copper sulphate, copper chloride, sodium chloride, bromide, and sulphate were used in the same way. The results in volts are tabulated below and curves are plotted in Fig. 4.

Curve.	Conc. →	∞	0.15	0.20	0.25	0.30
A	NaCl	+0.28		+0.10		
B	$CuSO_4$	+0.28+		+0.30		
C	$CuCl_2$	+0.28+			+0.33−	
D	$CuCl_2$	+0.28			+0.32	
E	NaCl	+0.29	+0.10			+0.07
F	Na_2SO_4	+0.29	+0.22−			+0.20−
G	NaBr	+0.28	+0.06			+0.03
H	$CuSO_4$	+0.28+	+0.35			+0.37−

Curve.	Conc. →	0.40	0.50	0.60	1.00
A	NaCl	+0.05			+0.01−
B	$CuSO_4$	+0.31−			+0.31−
C	$CuCl_2$		+0.33		+0.30
D	$CuCl_2$		+0.33+		+0.30
E	NaCl			+0.05+	+0.04−
F	Na_2SO_4			+0.19−	+0.19
G	NaBr			+0.00+	−0.02+
H	$CuSO_4$			+0.36	+0.36−

A and *E* were made with entirely different solutions, as were also *B* and *H*. *C* and *D* were made with solutions diluted from the same stock solution, but otherwise they are entirely separate. The two curves differ at no point by a hundredth of a volt. *F* and *G* were not repeated.

We see in these results much better duplication of readings than was possible before, but the discrepancies are still quite large and it does not yet seem advisable to compute and tabulate values of $L_1L_2 + L_2a$

$-L_1a$. To do so before the causes of the discrepancies are better understood would be to add to an already confusing mass of more or less conjectural data of doubtful value.

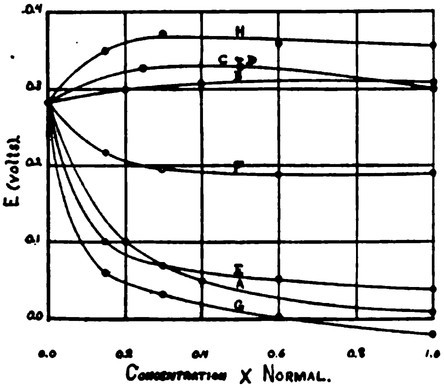

Fig. 4.

The following concentration cells were set up and the electromotive force measured with the potentiometer.

Cu-Na_2SO_4 (n)–NaCl (n)-Cu	0.164 volt.
Cu-$CuCl_2$ (n)–$CuSO_4$ (n)-Cu	0.004
Cu-$CuSO_4$ (n)–NaCl (n)-Cu	0.27
Cu-$CuSO_4$ (n)–NaBr (n)-Cu	0.35
Cu-Na_2SO_4 (n)–NaBr (n)-Cu	0.208

Combining these with the values of E taken from the curves we have the following table.

The Following Has	To the Following	A Contact P.D. in Volts.
$Na_2SO_4(n)$	$NaCl(n)$	+0.01 −0.02
$CuSO_4(n)$	$CuCl_2(n)$	−0.01
$CuSO_4(n)$	$NaCl(n)$	−0.03 0.00
$CuSO_4(n)$	$NaBr(n)$	+0.02
$Na_2SO_4(n)$	$NaBr(n)$	0.00

These results are the differences of the two air-liquid contact potential differences plus the diffusion potential between the two solutions. This last, according to the electrochemists, is small for the solutions used. Then it would seem that the air-liquid contact potential differences for normal solutions with clean surfaces has approximately the same value for the solutions examined.

It was pointed out by Ayrton and Perry that if their experiments were performed in gases other than air the question of air-liquid contact potential differences could be solved. Their apparatus would have given differential results, however, and would have left the question of gas-liquid contact potential differences unanswered. With the writer's apparatus this problem may be more easily attacked, and if the surface potential of the condenser plate does not change when immersed in different gases, the difference of the gas-liquid potential difference for different gases may be directly observed.

At best experimental work in this field is tedious. Slight impurities in the water used in making the solutions seem to have considerable effect especially with solutions of low concentration. Distilled water of the best quality and in quantity sufficient for work of this kind could not be had, and it is possible that the discrepancies still in evidence may be traceable to this cause. It is the writer's intention to so modify the apparatus that a much smaller quantity of solution will suffice, and to investigate further the questions that have arisen.

The writer's thanks are due to Professors Sanford and Rogers for their kindly suggestions and criticism during the progress of the work.

SUMMARY.

1. Contact potential differences with liquids have been studied by means of the inductive method.

2. The general existence of a potential difference at the air-liquid contact has been definitely shown.

3. The air-liquid contact potential difference may vary as much as three tenths of a volt, depending on the condition of the liquid surface.

4. Water and the aqueous solutions used are more positive to the air when the surface is clean than when it is contaminated.

5. The value of the air-liquid contact potential difference (for the solutions studied) is approximately the same for aqueous solutions of different salts at normal concentration.

STANFORD UNIVERSITY,
April, 1913.

ON THE ELEMENTARY ELECTRICAL CHARGE AND THE AVOGADRO CONSTANT.

BY R. A. MILLIKAN.

I. INTRODUCTORY.

THE experiments herewith reported were undertaken with the view of introducing certain improvements into the oil-drop method[1] of determining e and N and thus obtaining a higher accuracy than had before been possible in the evaluation of these most fundamental constants.

In the original observations by this method such excellent agreement was found between the values of e derived from different measurements (l. c., p. 384) that it was evident that if appreciable errors existed they must be looked for in the constant factors entering into the final formula rather than in inaccuracies in the readings or irregularities in the behavior of the drops. Accordingly a systematic redetermination of all these constants was begun some three years ago. The relative importance of the various factors may be seen from the following review.

As is now well known the oil-drop method rested originally upon the assumption of Stokes's law and gave the charge e on a given drop through the equation

$$e_n = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{\frac{3}{2}}\left(\frac{1}{g(\sigma-\rho)}\right)^{\frac{1}{2}}\frac{(v_1+v_2)v_1^{\frac{1}{2}}}{F}, \tag{1}$$

in which η is the coefficient of viscosity of air, σ the density of the oil, ρ that of the air, v_1 the speed of descent of the drop under gravity and v_2 its speed of ascent under the influence of an electric field of strength F.

The essential feature of the method consisted in repeatedly changing the charge on a given drop by the capture of ions from the air and in thus obtaining a series of charges with each drop. These charges showed a very exact multiple relationship under all circumstances—a fact which demonstrated very directly the atomic structure of the electric charge. If Stokes's law were correct the greatest common divisor of this series of charges should have been the absolute value of the elementary electrical charge. But the fact that this greatest common divisor failed to come out a constant when drops of different sizes were used showed that Stokes's law breaks down when the diameter of a drop begins to approach the order of magnitude of the mean free path of a gas molecule. Consequently the following corrected form of Stokes's law for the speed of a drop falling under gravity was suggested.

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[1] R. A. Millikan, PHYS. REV., 32, pp. 349–397, 1911.

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}\left\{1 + A\frac{l}{a}\right\}, \tag{2}$$

in which a is the radius of the drop, l the mean free path of a gas molecule and A an undetermined constant. It is to be particularly emphasized that the term in the brackets was expressly set up merely as a first order correction term in *l/a and involved no theoretical assumptions of any sort;* further that *the constant A was empirically determined* through the use only of small values of l/a and that *the values of e and N obtained were therefore precisely as trustworthy as were the observations themselves.* This fact has been repeatedly overlooked in criticisms of the results of the oil-drop method.[1]

Calling then e_1 the greatest common divisor of all the various values of e_n found in a series of observations on a given drop there resulted from the combination of (1) and (2) the equation

$$e\left(1 + A\frac{l}{a}\right)^{\frac{3}{2}} = e_1, \tag{3}$$

or

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[1] Indeed M. Jules Roux (Compt. Rendu, 152, p. 1168, May, 1911) has attempted to correct my values of e and N by reducing some observations like mine which he made on droplets of sulphur, with the aid of a purely theoretical value of A which is actually approximately twice too large. The impossibility of the value of A which he assumes he would himself have discovered had he made observations on spheres of different sizes or at different pressures. Such observations whether made on solid spheres or on liquid spheres always yield a value of A about half of that assumed by Roux. Hence his value of e, viz., $e = 4.17 \times 10^{-10}$ rests on no sort of experimental foundation whatsoever. It rests rather on two erroneous assumptions, first the assumption of the correctness of the constants in Cunningham's theoretical equation (Proc. Roy. Soc., 83, p. 357; see also footnote 3, p. 380, Phys. Rev., Vol. 32)—constants which I shall presently show are in no case correct within the limits of experimental error even when inelastic impact is assumed, and second, the assumption that molecules make elastic impact against solid surfaces, an assumption which is completely incorrect as I had already proved by showing that the value of the "slip" term is the same for oil and air as for glass and air (Phys. Rev., Vol. 32, p. 382), which Knudsen also had proved experimentally to be erroneous (Knudsen, An. der Phys., 28, p. 75, 1909, and 35, p. 389) and which for theoretical reasons as well is plainly inadmissible, since were it correct Poiseuille's law could not hold for gases under any circumstances.

But even if Roux had assumed the correct value of A he would still have obtained results several per cent. too low, a fact which must be ascribed either to faulty experimental arrangements or to imperfect knowledge of the density of his sulphur spheres; *for solid spheres have been very carefully studied in the Ryerson Laboratory and are in fact found to yield results very close to those obtained with oil drops.* Solid spheres however are not nearly so well adapted to a precision measurement of e as are oil drops, since their density and sphericity are always matters of some uncertainty.

$$e = \frac{e_1}{\left(1 + A\frac{l}{a}\right)^{\frac{3}{2}}}. \tag{4}$$

It was from this equation that e was obtained after A had been found by a graphical method which will be more fully considered presently.

The factors then which enter into the determination of e are: (1) The density factor, $\sigma - \rho$; (2) the electric field strength, F; (3) the viscosity of air, η; (4) the speeds, v_1 and v_2; (5) the drop radius, a; (6) the correction term constant, A.

Concerning the first two of these factors little need be said unless a question be raised as to whether the density of such minute oil drops might not be a function of the radius. Such a question is conclusively answered in the negative both by theory[1] and by the experiments reported in this paper.

Liquid rather than solid spheres were originally chosen because of the far greater certainty with which their density and sphericity could be known. Nevertheless I originally used liquids of widely different viscosities (light oil, glycerine, mercury) and obtained the same results with them all within the limits of error, thus showing experimentally that so far as this work was concerned, the drops all acted like rigid spheres. More complete proof of this conclusion is furnished both by the following observations and by other careful work on solid spheres soon to be reported in detail by Mr. J. Y. Lee.

The material used for the drops in the following experiments was the highest grade of clock-oil, the density of which, at 23° C., the temperature

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[1] The pressure p_2 within an oil drop is given by

$$p_2 = k + \frac{\alpha}{2R}$$

where k is LaPlace's constant of internal pressure, α the constant of surface tension and R the radius. The difference $(p_2 - p_1)$ between the pressure within the oil drop and within the oil in bulk is then $\alpha/2R$. But the coefficient of compressibility of a liquid is defined by

$$\beta = \frac{v_2 - v_1}{v_1(p_2 - p_1)}.$$

Now β for oil of this sort never exceeds 70×10^{-6} megadynes per sq. cm. (see Landolt and Bornstein's tables), while α is about 35 dyne cm. R for the smallest drop used (Table XX.) is .00005 cm.; we have then

$$\frac{v_2 - v_1}{v_1} = \beta\frac{\alpha}{2R} = \frac{70 \times 10^{-12} \times 35}{.0001} = .000024.$$

The density of the smallest drop used is then 2 parts in 100,000 greater than that of the oil in bulk. The small drops could then only be appreciably denser than the larger ones if the oil were inhomogeneous and if the atomizing process selected the heavier constituents for the small drops. Such an assumption is negatived by the experimental results given in § 9.

at which the experiments were carried out, was found in two determinations made four months apart, to be .9199 with an error of not more than one part in 10,000.

The electric fields were produced by a 5,300-volt storage battery, the P.D. of which dropped on an average 5 or 10 volts during an observation of an hour's duration. The potential readings were taken, just before and just after a set of observations on a given drop, by dividing the bank into 6 parts and reading the P.D. of each part with a 900-volt Kelvin and White electrostatic voltmeter which showed remarkable constancy and could be read easily, in this part of the scale, with an accuracy of about 1 part in 2,000. This instrument was calibrated by comparison with a 750-volt Weston Laboratory Standard Voltmeter certified correct to 1/10 per cent. and actually found to have this accuracy by comparison with an instrument standardized at the Bureau of Standards in Washington. The readings of P.D. should therefore in no case contain an error of more than 1 part in 1,000. As a matter of fact 5,000 volt readings made with the aid of two different calibration curves of the K. & W. instrument made two years apart never differed by more than 1 or 2 parts in 5,000.

The value of F involves in addition to P.D. the distance between the plates, which was as before 16 mm. and correct to about .01 mm. (l. c., p. 351). Nothing more need be said concerning the first two of the above-mentioned factors. The last four however need especial consideration.

2. THE COEFFICIENT OF VISCOSITY OF AIR.

This factor certainly introduces as large an element of uncertainty as inheres anywhere in the oil-drop method. Since it appears in equation (1) in the 3/2 power an uncertainty of 0.5 per cent. in η means an uncertainty of 0.75 per cent. in e. It was therefore of the utmost importance that η be determined with all possible accuracy. Accordingly two new determinations were begun three years ago in the Ryerson Laboratory, one by Mr. Lachlan Gilchrist and one by Mr. I. M. Rapp. Mr. Gilchrist, whose work has already been published,[1] used a constant deflection method (with concentric cylinders), which it was estimated (l. c., p. 386) ought to reduce the uncertainty in η to 1 or 2 tenths of a per cent. The results have justified this estimate. Mr. Rapp used a form of the capillary tube method which it was thought was better adapted to an *absolute evaluation of* η than have been the capillary tube arrangements which have been commonly used heretofore.[2] Since Mr.

[1] Lachlan Gilchrist, PHYS. REV., 2d Ser., Vol. 1, p. 124.

[2] This investigation will shortly be published in full (PHYS. REV., 1913), hence only a bare statement will here be made of the results which are needed for the problem in hand.

Gilchrist completed his work at the University of Toronto, Canada, and Mr. Rapp made his computations and final reductions at Ursinus College, Pa., neither observer had any knowledge of the results obtained by the other. The two results agree within 1 part in 600. Mr. Rapp estimates his maximum uncertainty at 0.1 per cent., Mr. Gilchrist at 0.2 per cent. Mr. Rapp's work was done at 26° C. and gave $\eta_{26} = .00018375$. When this is reduced to 23° C., the temperature used in the following work, by means of formula (5)—a formula[1] which certainly can introduce no appreciable error for the range of temperature here used,—viz.,

$$\eta_t = 0.00018240 - 0.000000493(23 - t); \tag{5}$$

there results

$$\eta_{23} = .00018227.$$

Mr. Gilchrist's work was done at 20.2° C. and gave $\eta_{20.2} = .0001812$. When this is reduced to 23° C. it yields

$$\eta_{23} = .00018257.$$

When this new work, by totally dissimilar methods, is compared with the best existing determinations by still other methods the agreement is exceedingly striking. Thus in 1905, Hogg[2] made at Harvard very careful observations on the damping of oscillating cylinders and obtained in three experiments at atmospheric pressure $\eta_{23} = 0.0001825$, $\eta_{15.6} = 0.0001790$ and $\eta_{18.6} = 0.0001795$. These last two reduced to 23° C., as above, are 0.0001826 and 0.0001817 respectively and the mean value of the three determinations is

$$\eta_{23} = 0.00018227.$$

Tomlinson's classical determination,[3] by far the most reliable of the nineteenth century, yielded when the damping was due primarily to "push" $\eta_{12.69^\circ \text{C}} = 0.00017746$; when it was due wholly to "drag" $\eta_{11.79^\circ \text{C}} = 0.00017711$. These values reduced to 15° C., as above, are respectively 0.00017862 and 0.00017867. Hence we may take Tomlinson's direct determination as $\eta_{15} = 0.00017864$. This reduced to 23° C. by Tomlinson's own temperature formula (Holman's) yields $\eta_{23} = 0.00018242$. By the above formula it yields $\eta_{23} = 0.00018256$.

Grindley and Gibson using the tube method on so large a scale[4] (tube 1/8 inch in diameter and 108 feet long) as to largely eliminate the most fruitful sources of error in this method, namely, the smallness and ununiformity of the bore, obtained at room temperature the following results:[1] $\eta_{25.28° \text{C.}} = .00018347$, $\eta_{23.55° \text{C.}} = .00018241$, $\eta_{12.18° \text{C.}} = .00018257$, and $\eta_{15.4° \text{C.}} = .0001782$. These numbers, reduced to 23° C. as above, are respectively 18,245, 18,241, 18,201, and 18,195. The mean is 18,220. Grindley and Gibson's own formula, $\eta = .0001702 \{1 + .00329t - .0000070t^2\}$, yields $\eta_{23} = .00018245$. We may take then Grindley and Gibson's direct determination as the mean of these two values, viz.: $\eta_{23} = .00018232$.

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[1] See R. A. Millikan, Annalen der Physik, 1913, for a more extended discussion of this and other viscosity formulæ and measurements.

[2] J. L. Hogg, Proc. Amer. Acad., 40, 18, p. 611, 1905.

[3] Tomlinson, Phil. Trans., 177, p. 767, 1886.

[4] Grindley and Gibson, Proc. Roy. Soc., 80, p. 114, 1908.

Collecting then the five most careful determinations of the viscosity of air which so far as I am able to discover have ever been made we obtain the following table.

TABLE I.

Air η_{23} = .00018227—Rapp. Capillary tube method. 1913.
Air η_{23} = .00018257—Gilchrist. Constant deflection method. 1913.
Air η_{23} = .00018227—Hogg. Damping of oscillating cylinder method. 1905.
Air η_{23} = .00018258—Tomlinson. Damping of pendular vibrations method. 1886.
Air η_{23} = .00018232—Grindley and Gibson. Flow through large pipe method. 1908.
Mean = .00018240

It will be seen, then, that every one of the five different methods which have been used for the absolute determination of η *leads to a value which differs by less than 1 part in 1,000 from the above mean value* $\eta_{23} = .00018240$. *It is surely legitimate then to conclude that the absolute value of* η *for air is now known with an uncertainty of somewhat less than 1 part in 1,000.*[2]

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[1] These numbers represent the reduction to absolute C.G.S. units of all the observations which Grindley and Gibson made between 50° F. and 80° F.

[2] In obtaining the above mean I have chosen what, after careful study, I have considered to be the best determination by each of the five distinct methods. The transpiration method has been much more commonly used than have the others, and in general, the final result is in good agreement with other careful work by this method. Thus Rankine's final value (Proc. Roy. Soc., *A*, 83, p. 522, 1910) by a new modification of the capillary tube method, while probably not claiming an accuracy of more than .4 per cent., is, at 10.6° C., .0001767, a value which reduces to $\eta_{23} = .0001828$. Again Fisher's final formula (PHYS. REV., 28, p. 104, 1909) gives $\eta_{23} = .00018218$. Also Holman's much used formula (Phil. Mag., 21, p. 199, 1886, and Tomlinson, Phil. Trans., Vol. 177, part 2, p. 767, 1886) yields $\eta_{23} = .00018237$. In fact the only reliable work on η which I am able to find which is out of line with the value $\eta_{23} = .00018240$ is that by Breiterbach at Leipzig (Ann. der Phys., 5, p. 166, 1901) and that by Schultze (Ann. der Phys., 5, p. 157, 1901) and several other observers at the University of Halle who used Schultze's apparatus (Markowski, Ann. der Phys., 14, p. 742, 1904, and Tanzler, Verh. der D. Phys. Ges., 8, p. 222, 1906). None of these observers however were aiming at an absolute determination, but rather at the effects of temperature and the mixing of gases upon viscosity and their capillaries were too small (of the order .007 cm.) to make possible an absolute determination of high accuracy. Their agreement among themselves upon a value which is about 1.3 per cent. too high is partly accounted for by the fact that several of them used the same tube. None of them made any effort to eliminate the necessarily large error in the measurement of so small a bore (which appears in the result in the fourth power) by taking the mean of η from a considerable number of tubes.

A second question which might be raised in connection with η is as to whether the medium offers precisely the same resistance to the motion through it of a heavily charged drop as to that of an uncharged drop. This question has been carefully studied and definitely answered in the affirmative by the following work (cf. §§ 6 and 10).

3. The Speeds v_1 and v_2.

The accuracy previously attained in the measurement of the times of ascent and descent between fixed cross-hairs was altogether satisfactory, but the method which had to be employed for finding the magnifying power of the optical system, *i. e.*, for finding the actual distance of fall of the drop in centimeters, left something to be desired. This optical system was before a short-focus telescope of such depth of focus that it was quite impossible to obtain an accurate measure of the distance between the cross-hairs by simply bringing a standard scale into sharp focus immediately after focusing upon a drop. Accordingly, as stated in the original article, the standard scale was set up at the exact distance from the telescope of the pin-hole through which the drop entered the field. This distance could be measured with great accuracy but *the procedure assumed that the drop remained exactly at this distance throughout the whole of any observation, sometimes of several hours duration.* But if there were the slightest lack of parallelism between gravity and the lines of the electric field the drop would be obliged to drift slowly, and always in the same direction, away from this position, and a drift of 5 mm. was enough to introduce an error of 1 per cent. Such a drift could in no way be noticed by the observer if it took place in the line of sight; for the speeds of the drops were changing *very slowly* anyway because of evaporation, fall in the potential of the battery, etc., and a change in time due to such a drift would be completely masked by other causes of change. This source of uncertainty was well recognized at the time of the earlier observations and steps were taken at the beginning of the present work to eliminate it. It was in fact responsible for an error of nearly two per cent.

A new optical system was built, consisting of an achromatic objective of 28 mm. aperture and 12.5 cm. focal length and an eyepiece of 12 mm. focal length. The whole system was mounted in a support which could be moved bodily back and forth by means of a horizontal screw of ½ mm. pitch. In an observation the objective was 25 cm. distant from the drop, which was kept continually in sharp focus by advancing or withdrawing the whole telescope system. The depth of focus was so small that a motion of ½ mm. blurred badly the image of the drop. The eyepiece was provided with a scale having 80 horizontal divisions and the distance between the extreme divisions of this scale (the distance of fall in the following experiments) could be regularly duplicated with an accuracy of at least 1 part in 1,000, by bringing a standard scale (Société Genevoise) into sharp focus. (The optical path when the scale was viewed was made exactly the same as when the drop was viewed.) The distance of fall, then, one of the most uncertain factors of the preceding determination, was now known with at least this degree of precision.

The accuracy of the *time* determinations can be judged from the data in Tables IV.–XIX. On account of the great convenience of a direct-reading instrument these time measurements were all made, not with a chronograph, as heretofore, but with a Hipp chronoscope which read to 0.002 second. This instrument was calibrated by comparison with the standard Ryerson Laboratory clock under precisely the same conditions as those under which it was used in the observations themselves and found to have an error between 0 and 0.2 per cent. depending upon the time interval measured. For the sake of enabling others to check all the computations herein contained if desired, as well as for the sake of showing what sort of consistency was attained in the measurement of time intervals there are given in Table II. the calibration readings for the 30 sec. interval and in Table III. the results of similar readings for all the intervals used.

TABLE II.

Chronoscope Readings for 30 Sec. Interval.	
29.962	29.990
29.988	29.958
29.986	29.920
29.930	29.972
29.964	29.976
30.002	30.006
29.940	29.979
29.998	30.018
29.930	29.926
29.967	29.972
Corr'n = +.1 per cent.	

TABLE III.

Clock Interval, Sec.	Chronoscope Interval.	Corr'n Applied, Per Cent.
6	6.0146	−0.26
10	10.0018	0.00
16	16.0080	0.00
20	19.9835	+0.07
30	29.9695	+0.10
40	39.9436	+0.14
60	59.9072	+0.16
114	113.795	+0.20
120	119.782	+0.20

The change in the per cent. correction with the time interval employed is due to the difference in the reaction times of the magnet and spring contact at make (beginning) and at break (end). All errors of this sort are obviously completely eliminated by making the calibration observations under precisely the same conditions as the observations on the drop. In Tables IV. to XIX. the recorded times are the uncorrected chronograph readings. The corrections are obtained by interpolation in the last column of Table III.

Under the head of possible uncertainties in the velocity determinations are to be mentioned also the effects of a distortion of the drop by the electric field. Such a distortion would increase the surface of the drop, and hence the speed imparted to it per dyne of *electric* force would not be the same as the speed imparted per dyne of gravitational force when the field was off and the drop had the spherical form. The following observations were made in such a way as to bring to light such an effect if it were of sufficient magnitude to exert any influence whatever upon the accuracy of the determination of e by this method (cf. §§ 6 and 10).

Similarly objection has been made to the oil-drop method on the ground that, on account of internal convection, fluid drops would not move through air with the same speed as solid drops of like diameter and mass. Such objection is theoretically unjustifiable in the case of oil drops of the sizes here considered.[1] Nevertheless the experimental demonstration of its invalidity is perhaps worth while and is therefore furnished below.

4. The Radius "*a*."

The radius of the drop enters only into the correction term (see equation 4) and so long as this is small need not be determined with a high degree of precision. It is most easily obtained by the following procedure which differs slightly from that originally employed (l. c., p. 379).

It will be seen that the equation (l. c., p. 353)

$$\frac{v_1}{v_2} = \frac{mg}{Fe - mg} \tag{6}$$

contains no assumption whatever save that a given body moves through a given medium with a speed which is proportional to the force acting upon it. Substitution in this equation of $m = \frac{4}{3}\pi a^3(\sigma - \rho)$ and the solution of the resulting equation for a gives

$$a = \sqrt[3]{\frac{3Fe}{4\pi g(\sigma - \rho)}\,\frac{v_1}{(v_1 + v_2)}}. \tag{7}$$

The substitution in this equation of an approximately correct value of e yields a with an error but one third as great as that contained in the assumed value of e. The radius of the drop can then be determined from (7) with a very high degree of precision as e becomes more and more accurately known. In the following work the value of e substituted in (7) to obtain a was 4.78×10^{-10} but the final value of e obtained would not have been appreciably different if the value substituted in (7) to obtain a had been 5 per cent. or 6 per cent. in error. The determination of a therefore introduces no perceptible error into the evaluation of e.

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[1] Hadamard, Compt. Rendus, 1911.

5. THE CORRECTION-TERM CONSTANT A.

This constant was before graphically determined (l. c., p. 379) by plotting the values of $e_1^{\frac{2}{3}}$ as ordinates and those of l/a as abscissæ and observing that if we let $x = l/a$, $y = e_1^{\frac{2}{3}}$ and $y_0 = e^{\frac{2}{3}}$ equation (3) may be written in the form

$$y_0(1 + Ax) = y \tag{8}$$

or

$$A = \frac{\frac{dy}{dx}}{y_0} = \frac{\text{slope}}{y \text{ intercept}}. \tag{9}$$

Now even if the slope were correctly determined by the former observations all of the above-mentioned sources of error would enter into the value of the intercept and hence would modify the value of A.

As a matter of fact however the accuracy with which the slope itself was determined could be much improved, for with the preceding arrangement it was necessary to make all the observations at atmospheric pressure and the only way of varying l/a was by varying a, *i. e.*, by using drops of different radii. But when a was very small the drops moved exceedingly slowly under gravity and the minutest of residual convection currents produced relatively large errors in the observed speeds, *i. e.*, in e_1. If for example the time of fall over a distance of 2 mm. is 20 minutes it obviously requires an extraordinary degree of stagnancy to prevent a drift in that time of say .2 mm. due to convection. But this would introduce an error of 10 per cent. into e_1. Furthermore with these slow drops Brownian movements introduce errors which can only be eliminated by taking a very large number of readings[1] and this is not in general feasible with such drops. It is quite impossible then by working at a single pressure to obtain from the graph mentioned above a line long enough (l. c., p. 379) to make the determination of its slope a matter of great precision. Accordingly in the new observations the variation of l/a was effected chiefly through the variation of l, *i. e.*, of the pressure p, rather than of a. This made possible not only the accurate evaluation of e, but also the solution of the interesting question as to the law of fall of a given drop through air at reduced pressures.

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[1] Fletcher, Phys. Rev., 33, p. 92, 1911.

6. METHOD OF TESTING THE ASSUMPTIONS INVOLVED IN THE OIL-DROP METHOD.

In order to make clear the method of treatment of the following observations a brief consideration of the assumptions underlying the oil-drop method must here be made. These assumptions may be stated thus:

1. The drag which the medium exerts upon a given drop is unaffected by its charge.

2. Under the conditions of observation the oil drops move through the medium essentially as would solid spheres. This assumption may be split into two parts and stated thus: Neither (2*a*) distortions due to the electric field nor (2*b*) internal convection within the drop modify appreciably the law of motion of an oil drop.[1]

3. The density of oil droplets is independent of their radius down to $a = .00005$ cm.

Of these assumptions (2*a*) is the one which needs the most careful experimental test.[2] It will be seen that it is contained in the fundamental equation of the method (see (7)) which may be written in the form

$$e_n = \frac{mg}{Fv_1}(v_1 + v_2). \tag{10}$$

Or still more conveniently in the form

$$e_n = \frac{mgt_g}{F}\left(\frac{1}{t_g} + \frac{1}{t_F}\right), \tag{11}$$

in which t_g and t_F are the respective time intervals required by the drop to fall under gravity and to rise under the field F the distance between the cross-hairs.

In order to see how the assumption under consideration can be tested let us write the corresponding equation after the same drop has caught n' additional units, namely,

$$e_{n+n'} = \frac{mgt_g}{F}\left(\frac{1}{t_g} + \frac{1}{t_F'}\right). \tag{12}$$

The subtraction of (11) from (12) gives

$$e_{n'} = \frac{mgt_g}{F}\left(\frac{1}{t_F'} - \frac{1}{t_F}\right). \tag{13}$$

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[1] M. Brillouin has in addition suggested (see p. 149, La Théorie du Rayonnement et les Quanta) that the drops may be distorted by the molecular bombardment, but Einstein's reply (l. c., p. 150) to this suggestion is altogether unanswerable, and, in addition, such a distortion, if it existed, would make the value of e given by the oil-drop method *too small* instead of too large.

[2] Professor Lunn has however subjected it to a theoretical study and has in this way demonstrated its validity (PHYS. REV., XXXV., p. 227, 1912).

Now equations (11) and (12) show, since mgt_g/F remains constant, that as the drop changes charge the successive values of its charge are proportional to the successive values assumed by the quantity $(1/t_g + 1/t_F)$ and the elementary charge itself is obviously this same constant factor mgt_g/F multiplied by *the greatest common divisor* of all these successive values. It is to be observed too that since $1/t_g$ is in these experiments generally large compared to $1/t_F$ the value of this greatest common divisor, which will be denoted by $(1/t_g + 1/t_F)_0$, is determined primarily by the time of fall *under gravity*, and is but little affected by the time in the field. On the other hand equation (13) shows that the greatest common divisor of the various values of $(1/t_F' - 1/t_F)$, which will be designated by $(1/t_F' - 1/t_F)_0$, when multiplied by the same constant factor mgt_g/F, is also the elementary electrical charge. In other words $(1/t_g + 1/t_F)_0$ and $(1/t_F' - 1/t_F)_0$ are one and the same quantity, but while the first represents essentially a speed measurement when the field is off, the second represents a speed measurement in a powerful electric field. If then the assumption under consideration is correct we have two independent ways of obtaining the quantity which when multiplied by the constant factor mgt_g/F is the elementary electrical charge, but if on the other hand the distortion of the drop by the field modifies the law of motion of the oil drop through the medium then $(1/t_g + 1/t_F)_0$ and $(1/t_F' - 1/t_F)_0$ will not be the same. Now *a very careful experimental study of the relations of* $(1/t_g + 1/t_F)_0$ and $(1/t_F' - 1/t_F)_0$ *shows so perfect agreement that no effect of distortion in changing measurably the value of e can be admitted.*[1] (See Tables IV. to XIX.)

Turning next to assumption (1), this can be tested in three ways, all of which have been tried with negative results. First a drop containing from one up to six or seven elementary charges can be completely discharged and its time of fall under gravity when uncharged compared with its time when charged. Second, the multiple relationships shown in the successive charges carried by a given drop may be very carefully examined. They cannot hold exactly if when the drop is heavily charged it suffers a larger drag from the medium than when it is lightly charged. Third, when drops having widely different charges and different masses are brought to the same value of l/a by varying the pressure, the value of e_1 (which is proportional to $(v_1 + v_2)_0$), should come out smaller for the heavily than for the lightly charged drops. The following observations show that this is not the case.

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[1] It may be pointed out in passing that the above discussion brings to light a method of obtaining e which is independent of a viscosity measurement; for $(1/t_F' - 1/t_F)_0$ can be obtained for a body which is heavy enough to be weighed upon a micro-balance. Such a body would fall so rapidly that $1/t_g$ could not be measured, but it could be computed from the measurement of $1/t_F'$ and $1/t_F$ and the equation $(1/t_g + 1/t_F)_0 = (1/t_F' - 1/t_F)_0$. Either (12) or (13) could then be solved for e after m had been determined by direct weighing. A consideration of the sources of error in this method shows however that it cannot be made as accurate as the present method which involves the coefficient of viscosity of air.

The last criterion is also a test for (2*b*) for if internal convection modifies the speed of fall of a drop as Perrin wishes to assume that it may,[1] it must play a smaller and smaller rôle as the drop diminishes in size, hence varying l/a by diminishing a cannot be equivalent to varying l/a by increasing l. In other words the value of e_1 obtained from work on a large drop at a low pressure should be different from that obtained from work on a small drop at so high a pressure that l/a has the same value as for the large drop.

Finally if the density of a small drop is greater than that of a large one (see assumption 3) then, for a given value of l/a, the small drop will show a larger value of e_1 than the large one inasmuch as the computation of e_1 is based on a constant value of σ. *The fact, then, that for a given value of l/a the value of e_1 actually comes out independent of the radius or charge of the drops shows conclusively either that no one of these possible sources of error exists, or else that they neutralize one another so that for the purposes of this experiment they do not exist.* That they do not exist at all is shown by the independent theoretical and experimental tests mentioned above. This removes I think every criticism which has been suggested of the oil-drop method of determining e and N.

7. Summary of Improvements in Method.

In order to obtain the consistency shown in the following observations it was found necessary to take much more elaborate precautions to suppress convection currents in the air of the observing chamber than had at first been thought needful.

To recapitulate, then, the improvements which have been introduced into the oil-drop method, consist in (1) a redetermination of η; (2) an improved optical system; (3) an arrangement for observing speeds at all pressures; (4) the more perfect elimination of convection; (5) the experimental proof of the correctness of all the assumptions underlying the method, viz., (*a*) that a charge does not alter the drag of the medium on the charged body; (*b*) that the oil drops act essentially like solid spheres; (*c*) that the density of the oil drops is the same as the density of the oil in bulk.

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[1] La Théorie du Rayonnement et les Quanta, p. 239—Rapports et Discussions de la Réunion tenue à Bruxelles, Novembre, 1911. Edited by Langevin and de Broglie. Gauthier-Villars.

8. THE EXPERIMENTAL ARRANGEMENTS.

The experimental arrangements are shown in Fig. 1. The brass vessel *D* was built for work at all pressures up to 15 atmospheres but since the present observations have to do only with pressures from 76 cm. down these were measured with a very carefully made mercury manometer *m* which at atmospheric pressure gave precisely the same reading as a standard barometer. Complete stagnancy of the air between the condenser plates *M* and *N* was attained first by absorbing all of the heat rays from the arc *A* by means of a water cell *w*, 80 cm. long, and a cupric chloride cell[1] *d*, and second by immersing the whole vessel *D* in a constant temperature bath *G* of gas-engine oil (40 liters) which permitted, in general, fluctuations of not more than .02° C. during an observation. This constant temperature bath was found essential if such consistency of measurement as is shown below was to be obtained. A long search for causes of slight irregularity revealed nothing so important as this and after the bath was installed all of the irregularities vanished. The atomizer *A* was blown by means of a puff of carefully dried and dust-free air introduced through the cock *e*. The air about the drop *p* was ionized

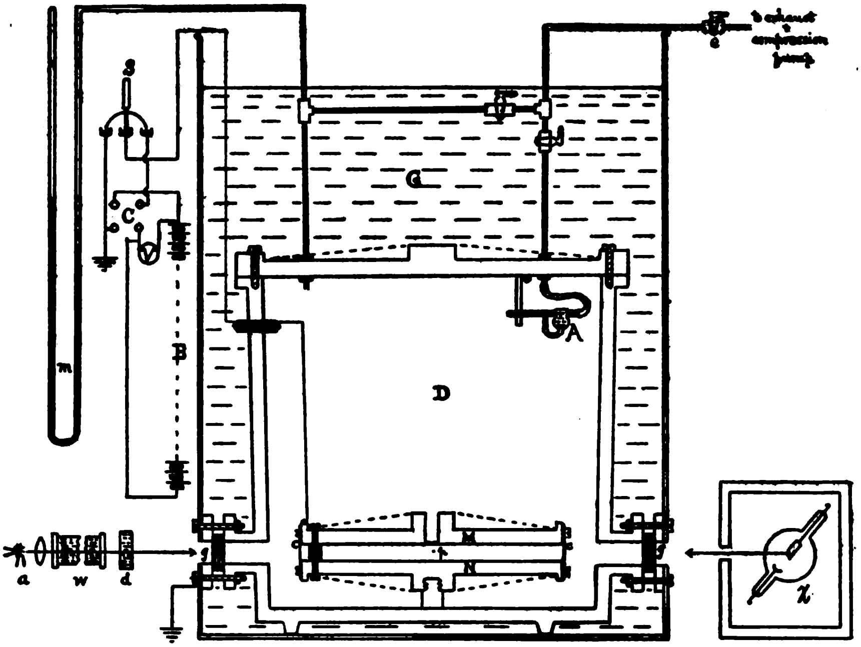

Fig. 1.

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[1] See Coblentz, Bulletin of the Bureau of Standards, Washington, D. C., Vol. 7, p. 660, 1911.

when desired by means of Röntgen rays from X which readily passed through the glass window g. To the three windows g (two only are shown) in the brass vessel D correspond, of course, three windows in the ebonite strip c which encircles the condenser plates M and N. Through the third of these windows, set at an angle of about 18° from the line Xpa and in the same horizontal plane, the oil drop is observed.

9. The Observations.

The record of a typical set of readings on a given drop is shown in Table IV. The first column, headed t_g, gives the successive readings on the time of descent under gravity. The fourth column, headed t_F, gives the successive times of ascent under the influence of the field F as measured on the Hipp chronoscope. These two columns contain all the data which is used in the computations. But in order to have a test of the stagnancy of the air a number of readings were also made with a stop-watch on the times of ascent through the first half and through the whole distance of ascent. These readings are found in the second and third columns, the times for the first half under the head $\frac{1}{2}t_{F_s}$, the times for the whole distance under the head t_{F_s}. It will be seen from these readings that there is no indication whatever of convection, since the readings for the one half distance have uniformly one half of the value of the readings for the whole distance, within the limits of error of a stop-watch measurement. This sort of a test was made on the majority of the drops, but since no further use is made of these stop-watch readings they will not be given in succeeding tables.

The fifth column, headed $1/t_F$, contains the reciprocals of the values in the fourth column after the correction found from Tables II. and III. has been applied. The sixth column contains the successive differences in the values of $1/t_F$ resulting from the capture of ions. The seventh column, headed n', contains the number of elementary units caught at each change, a number determined simply by observing by what number the quantity just before it in column 6 must be divided to obtain the constancy shown in the eighth column, which contains the successive determinations of $(1/t_F' - 1/t_F)_0$ (see § 6). Similarly the ninth column, headed n, gives the total number of units of charge on the drop, a number determined precisely as in the case of the numbers in the seventh column by observing by what numbers the successive values of $(1/t_g + 1/t_F)$ must be divided to obtain the constancy shown in the tenth column, which contains the successive values of $(1/t_g + 1/t_F)_0$. Since n' is always a small number and in some of the changes almost always has the value 1 or 2 its determination for any change is obviously never a matter of the slightest uncertainty. On the other hand, n is often a large number, but with the aid of the known values of n' it can always be found with absolute certainty so long as it does not exceed say 100 or 150. It will be seen from the means at the bottom of the eighth and the tenth columns that in the case of this drop the two ways discussed in § 6 of obtaining the number which when multiplied by mgt_g/F is the elementary electrical charge yield absolutely identical results.

TABLE IV.

Drop No. 6.

t_g Sec.	$\frac{1}{2}t_{F_s}$ Sec.	t_{F_s} Sec.	t_{F_c} Sec.	$\frac{1}{t_F}$	$\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$
11.848	39.9	80.2	80.708	.01236				18	.005366
11.890	11.2	22.4	22.366		.03234	6	.005390		
11.908			22.390	.04470				24	.005371
11.904	11.2	22.4	22.368		.03751	7	.005358		
11.882	70.6	140.4	140.565	.007192	.005348	1	.005348	17	.005375
11.906	39.9	79.6	79.600	.01254				18	.005374
11.838			34.748		.01616	3	.005387		
11.816			34.762	.02870				21	.005376
11.776			34.846						
11.840			29.286	.03414				22	.005379
11.904	14.6	29.3	29.236		.026872	5	.005375		
11.870	69.3	137.4	137.308	.007268	.021572	4	.005393	17	.005380
11.952	17.6	34.9	34.638	.02884				21	.005382
11.860					.01623	3	.005410		
11.846			22.104	.04507				24	.005386
11.912			22.268		.04307	8	.005384		
11.910			500.1	.002000				16	.005387
11.918			19.704	.05079	.04879	9	.005421	25	.005399
11.870			19.668		.03874	7	.005401		
11.888			77.630	.01285				18	.005390
11.894	38.9	77.6	77.806		.01079	2	.005395		
11.878	21.0	42.6	42.302	.02364				20	.005392
11.880					Means		**.005386**		**.005384**

Duration of exp. = 45 min.,
Plate distance = 16 mm.,
Fall distance = 10.21 mm.,
Initial volts = 5,088.8.
Final volts = 5,081.2.
Temperature = 22.82° C.,
Pressure = 75.62 cm.,
Oil density = .9199,
Air viscosity[1] = $1,824 \times 10^{-7}$,
Radius (a) = .000276 cm.,
l/a = .034,
Speed of fall = .08584 cm./sec.,
$e_1 = 4.991 \times 10^{-10}$.

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[1] **In the above and in all the following tables the computations were made on the basis of the assumption $\eta_{23} = 1{,}825 \times 10^{-7}$ instead of $\eta_{23} = 1{,}824 \times 10^{-7}$ (see § 2). The reduction to the latter value has been made only in the final value of e (see § 10).**

Table V.

Drop No. 16.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.638							
18.686							
18.689	17.756	.05628			16	.006853	
18.730	17.778		5	.006908			$V_i = 5106$
18.686	45.978	.02174			11	.006832	$V_f = 5100$
18.726	45.870						$t = 23.7°$ C.
18.772	45.716	.021826			8	.006851	$p = 74.68$
18.740	45.758		3	.006795			$v_1 = .05449$
18.724	694.0	.001441	5	.006860			$a = .0002188$
18.720	27.95	.03574	4	.006825	13	.006855	$l/a = .04390$
18.816	118.388	.008439	2	.006866	9	.006868	**$e_1 = 5.065$**
18.816	45.030	.02217			11	.006867	
18.716	34.564	.02890			12	.006856	
18.804	44.826	.02227	2	.006876	11	.006876	
18.746	117.198	.008518	2	.006889	9	.006876	
18.746	44.784	.022295			11	.006879	
18.790							
18.738				**.006860**		**.006861**	

Table VI.

Drop No. 14.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t'_F}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.606							
18.732							
18.784							
18.700	46.172	.02163			11	.006820	
18.730	17.896	.05600	5	.006874			$V_i = 5077$
18.652	17.818				16	.006833	$V_f = 5073$
18.656	46.328		5	.006886			$t = 23.09°$ C.
18.730	46.258	.02157			11	.006815	$p = 75.28$
18.760	46.266		1	.006803			$v_1 = .05451$
18.708	67.473						$a = .0002185$
18.658	67.148	.01484			10	.006823	$l/a = .04348$
18.668	67.148		6	.006840			**$e_1 = 5.064$**
18.826	17.896	.05588			16	.006831	
18.710	15.868	.06305			17	.006850	
18.802	15.854		9	.006853			
18.778	730.0	.001370	6	.006882	8	.006845	
18.790	23.376	.04266			14	.006861	
18.846	23.504		4	.006850			
18.804	65.416	.01526	1	.006871	10	.006865	
18.662	118.970	.008389	1	.006784	9	.006864	
18.704	622.8	.001605			8	.006874	
18.730				**.006850**		**.006844**	

In order to show the sort of consistency attained in this work the complete records are given in Tables V., VI., VII., VIII. and IX. of five drops of practically the same size, taken at very nearly the same pressures. These are the only drops of this size which were observed with the present arrangement so that they represent the regular run of observations rather than a selected group. The symbols in the last column V_i, V_f, t, p, v_1, and a stand for initial volts, final volts, temperature, pressure, velocity under gravity, and radius, respectively. It will be seen from the second columns (see Table V.) that in general in spite of the precautions taken against evaporation (l. c., p. 388) the drops do evaporate very slowly, since with a given charge the speed in the field very slowly increases. It is for this reason that the numbers in the next to the last column tend to increase very slightly. This slow change introduces no error into e_1, provided corresponding values of t_g, t_F and V (volts) are combined to obtain e_1. The mean values taken throughout the same time-interval constitute such corresponding values. On account of this slow change, however, the readings from which the differences $(1/t_F' - 1/t_F)$ are taken should be separated by as small a time interval as possible. It is for this reason that in Table V., for example, to obtain the difference $(1/t_F' - 1/t_F)$ corresponding to the change from $t_F = 45$ sec. to $t_F = 694$ sec.

TABLE VII.

Drop No. 18.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.626						
18.716						
18.602	21.206			15	.006716	
18.634	21.110	5	.006696			
18.694	72.590	2	.006820	10	.006726	$V_i = 5030$
18.678	36.454			12	.006742	$V_f = 5018$
18.598	48.870	2	.006735	11	.006725	$t = 23.0°$ C.
18.612	142.838	1	.006792	9	.006722	$p = 76.06$
18.622	72.428	2	.006732	10	.006729	$v_1 = .05463$
18.795	36.722					$a = .0002191$
18.732	36.652			12	.006729	$l/a = .04290$
18.780	36.602	3	.006719			$e_1 = 5.043$
18.736	140.891	2	.006799	9	.006732	
18.754	48.302					
18.712	48.266	4	.006756	11	.006745	
18.760	20.942			15	.006747	
18.716						
18.740						
18.695			**.006753**		**.006731**	

TABLE VIII.

Drop No. 18.

t_g	t_F	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.908				
18.948	14.348		.006801	
18.958	14.352	.006790		
18.950	45.070		.006813	
18.904	34.338			$V_t=5085$
18.988	34.432		.006816	$V_f=5071$
18.896	34.334			$t=23.83°$ C.
19.094	44.864			$p=75.24$
18.936	34.430	.006807		$v_1=.05274$
18.980	548.0	.006858	.00620	$a=.0002182$
19.030	34.14			$l/a=.04368$
18.872	44.654			$e_1=5.040$
18.808	44.520		.006831	
18.910	44.526			
18.946	64.28	.006766		
18.936	114.404			
18.950	113.452	.006751	.006834	
19.030	63.934	.006728	.006835	
19.116	23.260		.006832	
19.018	23.350			
18.959		.006817	.006823	

TABLE IX.

Drop No. 17.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.402						
18.556						$V_t=5065$
18.350	14.966					$V_f=5055$
18.470	14.870			18	.006752	$t=23.06°$ C.
18.412	37.376	6	.006727			$p=73.47$
18.318	37.594			12	.006748	$v_1=.05545$
18.388	37.368					$a=.0002209$
18.376	50.228	1	.006780	11	.006749	$e/a=.04411$
18.406	76.154	1	.006780	10	.006742	$e_1=5.054\times10^{-10}$
18.392	155.6	1	.006682	9	.006749	
18.492						
18.415			.006742		.006748	

the last two of the 45 sec. readings are averaged instead of the whole four. It is worthy of note, too, in this connection that if a change in the time in the field takes place first from 45 sec. to 694 sec. and then im-

TABLE X.

Drop No. 48.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
18.360						
18.362						
18.328	45.378			11	.006960	
18.444	45.208	6	.007027			
18.442	15.574			17	.006983	
18.330	17.468	6	.007011	16	.006983	$V_i=4240$
18.330	66.000			10	.006965	$V_f=4236$
18.428	66.020	1	.006993			$t=22.94°$ C
18.174	122.600	2	.006951	9	.006962	$p=15.72$ cm.
18.388	45.414					$v_1=.05564\frac{\text{cm.}}{\text{sec.}}$
18.392	45.282			11	.006960	
18.240	45.110					$a=.0002060$ cm.
18.314	45.282	2	.006911			$l/a=.2210$
18.324	121.600			9	.006971	$e_1=6.244\times10^{-10}$
18.312	121.200					
18.390						
18.347			**.006978**		**.006969**	

TABLE XI.

Drop No. 46.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
25.856	10.334			19	.007121	
25.946	10.342	10	.007086			
25.890	38.604	1	.007195	9	.007159	
25.876	53.450	3	.007152	8	.007154	
25.818	24.906			11	.007152	
25.934	30.248					$V_i=3406$
25.956	30.016	3	.007183	10	.007172	$V_f=3396$
25.876	18.282			13	.007174	$t=22.81°$ C.
26.064	16.216			14	.007159	$p=14.68$ cm.
26.018	24.860			11	.007161	$v_1=.03937$ cm.
25.902	21.062	2	.007155	12	.007168	$a=.0001690\frac{\text{cm.}}{\text{sec.}}$
25.860	30.126	2	.007155	10	.007171	
25.930	20.884					
25.994	21.130					$l/a=.2886$
25.814	21.174	5	.007170			$e_1=6.719\times10^{-10}$
26.012	85.922	1	.007198	7	.007167	
25.904	226.600	1	.007148	6	.007159	
25.802	86.368			7	.007174	
25.918	86.406					
25.816						
25.909			**.007160**		.007161	

mediately back again to the 45 second value the mean of the two values of $(1/t_F' - 1/t_F)$ thus obtained is independent of any error arising from the evaporation of the drop. For this reason the mean value of the quantity $1/n'(1/t_F' - 1/t_F)$ is in general much more trustworthy than might be inferred from the variation in the individual numbers from which this mean is obtained.

Table XII.

Drop No. 53.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
33.432	28.494			10	.006491	
33.346	28.624	2	.006501			$V_t = 2463$
33.172	20.806			12	.006493	$V_f = 2440.2$
33.310	20.832	3	.006503			$t = 23.16°$ C.
33.380	35.032	1	.006490	9	.006491	$p = 12.61$
33.306	28.548	4	.006505	10	.006491	$v_1 = .03055$
33.346	111.244	1	.006471	6	.006482	$a = .0001439$
33.328	400.000	1	.006436	5	.006485	$l/a = .3945$
33.684	111.706			6	.006475	$e_1 = 7.450 \times 10^{-10}$
33.484						
33.379			**.006484**		**.006487**	

Table XIII.

Drop No. 48.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
32.366	20.330	.04919			13	.006157	$V_t = 2561.$
32.398	23.140	.04313			12	.006165	$V_f = 2557.$
32.217	23.230		5	.006164			$t = 22.81°$ C.
32.342	80.786	.01231			7	.006166	$p = 15.35$ cm.
32.358	81.416		7	.006137			$v_1 = .03150$
32.438	18.113	.05517			14	.006144	$a = .0001501$ cm.
32.412	18.144		6	.006142			$l/a = .3104$
32.236	54.490	.01832			8	.006147	$e_1 = 6.866 \times 10^{-10}$
32.424	81.486	.01224	1	.006080	7	.006156	
32.356				.006131		.006156	

Nevertheless in practically all of the following work in view of the large number of observations in the t_g column, the mean at the bottom of the column $1/n(1/t_g + 1/t_F)$ is considered more trustworthy than the mean at the bottom of the column $1/n'(1/t_F' - 1/t_F)$ and it has been in fact exclusively used in the computation of e_1. Only in the case of 2 or 3 of the fastest drops (Tables XVI. and XVII.) are the uncertainties in

Table XIV.

Drop No. 47.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
12.836	11.960	.08369			42	.003840	
12.994	11.938						
12.892	10.704		13	.003812			
12.914	29.350						
12.930	29.280	.03411			29	.003851	
12.902	29.108						
12.838	32.866						$V_t=2555.$
12.808	33.068	.03034			28	.003854	$V_f=2545.$
12.920	32.894						$t=22.83°$ C.
12.886	32.892						$p=9.70$ cm.
12.908	29.204		5	.003858			$v_1=.07921$ cm./sec.
12.902	32.950						$a=.0002380$ cm.
12.916	90.040	.01108			23	.003855	$l/a=.3097$
12.850	90.152		1	.003860			$e_1=6.841\times10^{-10}$
12.854	66.762	.01496			24	.003854	
12.912	66.650		2	.003898			
12.908	139.8	.00716			22	.003852	
12.870	139.4		2	.003878			
12.882	66.942	.01492			24	.003855	
12.891				**.003861**		**.003852**	

Table XV.

Drop No. 41.

t_g	t_F	$\frac{1}{t_F}$	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
24.016	42.188						
24.142	42.078	.02369			8	.009336	
24.130	42.098		1	.009380			
24.070	69.900	.01431	1	.009389	6	.009328	$V_t=5065$
24.000	203.200	.004921	4	.009255	5	.009316	$V_f=5059$
24.030	23.844	.04194			9	.009286	$t=23.05°$ C.
24.046	30.606				8	.009289	$p=19.01$ cm.
24.028	42.800						$v_1=.04253$
23.968	42.944	.02326			7	.009276	$a=.0001816$
24.018	71.400	.01400	1	.009260	6	.009277	$l/a=.1394$
23.770			2	.009295			$e_1=6.097\times10^{-10}$
23.882	30.652	.03259				.009282	
24.008				**.009314**		**.009301**	

$(1/t_g + 1/t_F)_0$ greater perhaps than those in $(1/t_F' - 1/t_F)_0$ and in these cases the two were so near together that there was no object in using the latter instead of the former. It should be stated that all time intervals longer than 150 sec. were measured with the stop-watch rather than with the chronoscope and are not subjected to the corrections in Tables II. and III. In general, too, only differences in $t_F' - t_F$ amounting to as much as 20 seconds are used for the determination of $(1/t_F' - 1/t_F)$ since obviously the observational error is large when $t_F' - t_F$ is small.

Table XVI.

Drop No. 1.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_F'} - \frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g} + \frac{1}{t_F}\right)$	
	17.514			89	.003235	
	17.500	11	.003244			
.	46.724			78	.003233	
	46.494	10	.003216			
4.346	18.722			88	.003233	
4.400	18.616	11	.003256			
4.310	56.280			77	.003228	$V_i = 5174$
4.376	56.276	9	.003217			$V_f = 5162$
4.370	21.362			86	.003227	$t = 23.00°$ C.
4.422	21.476					$p = 75.80$ cm.
4.392						
4.290	58.936					$v_1 = .23565 \frac{\text{cm.}}{\text{sec.}}$
4.392	58.194			77	.003219	$a = .0005856$
4.360	58.456					$l/a = .01615$
4.346	58.904	10	.003199			$e_1 = 4.877 \times 10^{-10}$
4.368	20.412					
4.350	20.404			87	.003216	
4.363	20.322					
corrected to	10.710			101	.003211	
	10.660					
	20.290			87	.003218	
	20.296					
4.328[1]			.003226		.0032245	

A study of Tables IV. to IX. shows, *first*, a striking agreement between the values of $(1/t_F' - 1/t_F)_0$ and $(1/t_g + 1/t_F)_0$ the largest divergence being found in Table V. where it amounts to 0.3 per cent., and *second*, a satisfactory agreement between the values of e_1 obtained from the different drops of approximately the same size, the largest divergence from the mean value being here too 0.3 per cent.

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[1] These corrected times in Tables XVI. and XVII. are obtained by a slight extrapolation upon a calibration curve plotted from Table III. These two drops are the largest used and fall too rapidly for the most accurate work, but were introduced so as to test as thoroughly as possible the assumptions that even the largest of these drops fall like rigid spheres and that heavily charged drops experience no more drag from the medium than do uncharged ones. The drop of Table XVII. is evaporating more rapidly than any other used (see column t_F), probably because of the low pressure (4.46 cm.), hence the fourth column numbers are here obtained only from immediately adjacent observations in the second column. Each of these fourth column numbers shows the influence of the evaporation, but it is interesting to see how it is eliminated from the mean.

TABLE XVII.

Drop No. 56.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
5.092	19.480					
5.010	19.356			136	.001837	
5.082	19.374					
5.044	19.202					
——	29.214			127	.001832	
	29.022					
5.044	28.686					$V_i=1701$
5.030	38.688			122	.001839	$V_f=1699$
	38.620	7	.001786			$t=23.21°$ C.
5.066	75.136					$p=4.46$ cm.
5.120	73.752			117	.001811	$v_1=.20256$
5.046	72.758	9	.001837			$a=.0003653$ cm.
5.128	33.034			126	.001814	
4.912	32.788					$l/a=.4396$
5.036	39.956			123	.001814	$e_1=7.777\times10^{-10}$
5.080	46.790	5	.001796	121	.001814	
5.122	80.820			116	.001816	
5.058	80.152	3	.001877			
cor'd to	55.206	6	.001823	119	.001810	
	34.398			125	.001818	
5.039[1]			.001824		.001821	

TABLE XVIII.

Drop No. 22.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
40.518	17.760	4	.01012	8	.01012	
40.522	63.100			3	.01015	$V_i=5009$
40.382						$V_f=5001$
40.542						$t=23.22°$ C.
40.650	15.138			9	.01009	$p=76.42$ cm.
40.696	27.716			6	.01011	$v_1=.02515$
40.478	15.060	4	.01011	9		$a=.0001475$
40.458	38.606			5	.01012	$l/a=.06350$
40.494	38.382	2	.01008			$e_1=5.168\times10^{-10}$
40.802	172.626				.01013	
40.542			.01010		.01012	

A few typical records of observations made at different pressures (see "*p*," last column) and on drops of different sizes (see "*a*," last column) are presented in Tables X to XIX.

Table XIX.

Drop No. 52.

t_g	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_F'}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$	
50.364						$V_i = 3362$
50.442	44.446	1	.010515	4	.010566	$V_f = 3340$
50.416	30.254			5	.010556	$t = 22.98$
50.770	30.326					$p = 16.95$
50.178	22.904			6	.010575	$v_1 = .020216$
50.456	30.396	2	.01047	5	.010532	$a = .0001183$
50.460	83.716	1	.010664	3	.010573	$l/a = .3568$
50.118	796.000			2	.010528	$e_1 = 7.210 \times 10^{-10}$
50.400			.01055		.010555	

Table XX. contains a complete summary of the results obtained on all of the 58 different drops upon which complete series of observations like the above were made during a period of 60 consecutive days. It will be seen from this table that these observations represent a 30-fold variation in l/a (from .016, drop No. 1, to .444, drop No. 58), a 17-fold variation in p (from 4.46 cm., drop No. 56, to 76.27 cm., drop No. 10), a 12-fold variation in a (from 4.69×10^{-5} cm., drop No. 28, to 58.56×10^{-5} cm., drop No. 1) and a variation in the number of free electrons carried by the drop from 1 on drop No. 28 to 136 on drop No. 56. The time of fall of drop No. 28 was also tested when it was completely discharged, as have been the times of many other drops which carried most of the time but one electron.

Much larger variations both in a and p, and therefore in l/a, might have been used, and have in fact been used, for finding the law of fall of a drop through rarefied air, but for the end here sought, namely, the most accurate possible determination of e, it was found desirable to keep the t_g interval for the most part between the limits 10 sec. and 40 sec., in order to avoid chronograph errors on the one hand and Brownian movement irregularities on the other. That neither of these sources of error is appreciable in these observations may be seen from a study of Tables IV.–XIX., which are thoroughly representative of the work on all the drops.

10. Results and Discussion.

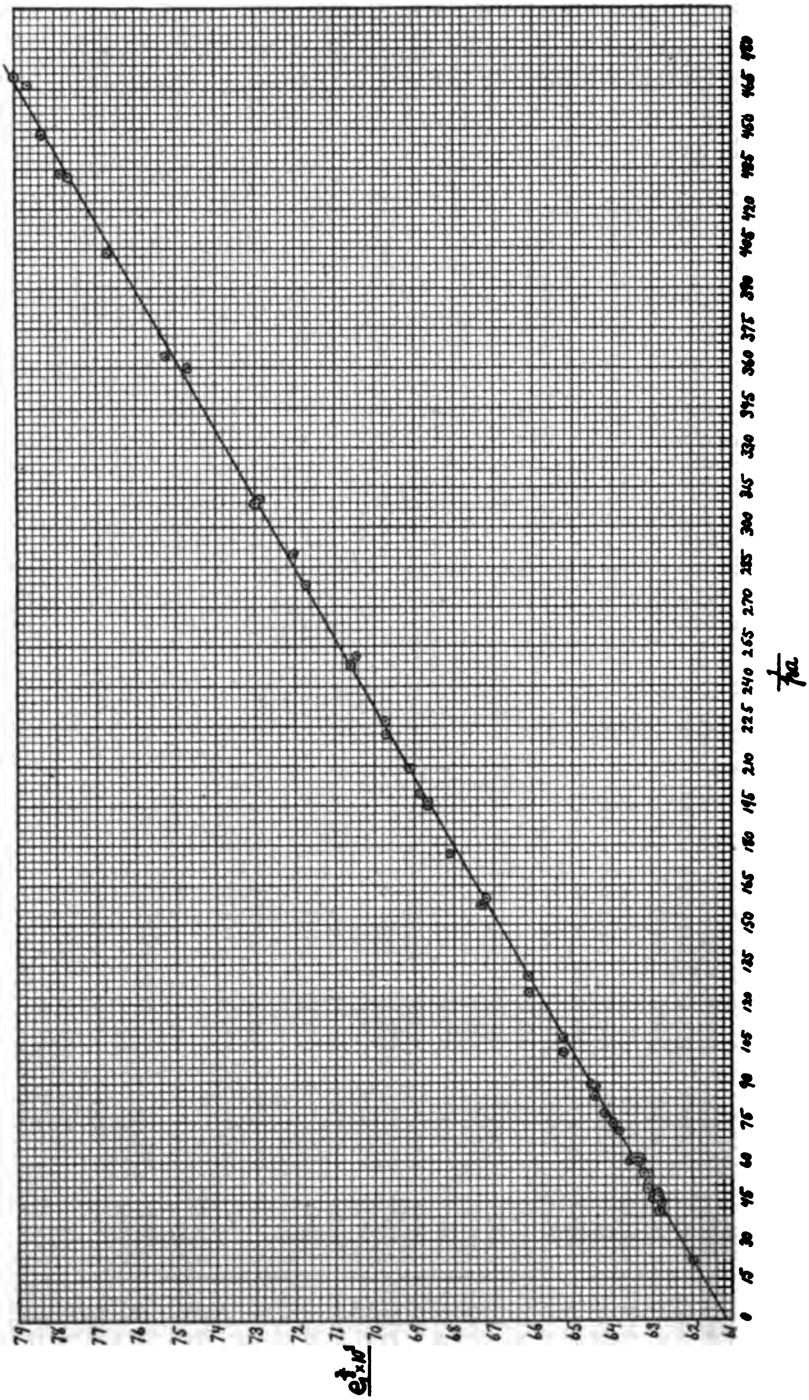
It will be seen at once from equation (4) that the value of e is simply the value of e_1 for which $l/a = 0$, so that if successive values of $e_1^{\frac{2}{3}}$ are plotted as abscissæ and of l/a as ordinates the intercept of the resulting curve on the $e_1^{\frac{2}{3}}$ axis is $e^{\frac{2}{3}}$. Furthermore if A is a constant then the curve in question is a straight line and A is the slope of this line divided by the

TABLE XX.

No.	Tem. °C.	P.D. (Volts).	t_g (Sec.).	V_1 cm./sec.	$(V_1+V_2)_0$	n	$a\times10^5$ cm.	p (cm. Hg).	$1/pa$	l/a	$e_1\times10^{10}$	$e_1^{\frac{2}{3}}\times10^8$	$e^{\frac{2}{3}}\times10^8$	
1	23.00	5,168	4.363	.2357	.003293	77–102	58.56	75.80	22.52	.01615	4.877	61.90	61.14	Mean = 61.120
2	22.80	5,120	8.492	.1202	.004670	27–36	32.64	75.00	40.85	.02933	4.981	62.82	61.26	
3	23.46	5,100	9.905	.1032	.004996	22–27	30.29	73.71	44.88	.03212	4.971	62.75	61.04	
4	22.85	5,163	10.758	.09489	.005211	18–36	28.94	75.20	45.92	.03288	5.001	63.00	61.24	
5	23.08	5.072	10.663	.09575	.005176	20–30	29.14	73.25	46.85	.03353	4.982	62.82	61.13	
6	22.82	5,085	11.880	.08584	.005497	17–24	27.54	75.62	48.11	.03437	4.991	62.93	61.09	
7	23.79	5,090	11.950	.08368	.005480	19–22	27.57	75.10	48.44	.03466	4.981	62.82	61.07	
8	23.50	5,158	12.540	.08141	.005623	16–19	26.90	75.30	49.52	.03544	5.016	63.12	61.23	
9	22.87	5,139	13.562	.07375	.005962	19–23	25.71	75.00	51.73	.03702	5.016	63.13	61.15	
10	23.25	5,015	15.380	.06641	.006174	13–22	24.31	76.27	54.09	.03871	5.010	63.08	61.02	
11	23.01	5,066	15.193	.06720	.006087	11–14	24.36	73.90	55.52	.03973	5.015	63.12	61.00	
12	23.00	5,080	15.985	.06375	.006416	12–16	23.70	75.14	56.15	.04018	5.028	63.24	61.10	
13	23.00	5,024	15.695	.05463	.006873	9–15	21.91	76.06	59.94	.04290	5.043	63.35	61.06	
14	23.09	5,077	18.730	.05451	.006988	8–16	21.85	75.28	60.78	.04348	5.064	63.53	61.21	
15	23.85	5,078	18.959	.05274	.006966	8–18	21.78	75.24	61.03	.04368	5.040	63.33	61.07	
16	23.70	5,103	18.738	.05449	.007005	9–16	21.87	74.68	61.33	.04390	5.065	63.54	61.21	
17	23.06	5,060	18.415	.05545	.006890	9–18	22.06	73.47	61.69	.04411	5.054	63.43	61.00	
18	22.83	5,093	26.130	.03907	.008339	5–13	18.45	75.54	71.74	.05134	5.098	63.82	61.08	
19	22.95	5,033	28.568	.03570	.008651	5–9	17.63	75.87	74.77	.05350	5.120	64.00	61.12	
20	23.00	5,094	9.480	.10772	.005058	23–32	30.54	41.77	78.40	.05612	5.145	64.22	61.23	
21	23.08	5,018	35.253	.02893	.009660	4–11	15.80	74.32	85.08	.06089	5.166	64.36	61.11	
22	23.22	5,005	40.542	.02515	.010332	3–9	14.75	76.42	88.70	.06350	5.168	64.40	61.01	
23	22.76	5,098	39.900	.02554	.010510	3–6	14.85	75.40	89.35	.06395	5.190	64.59	61.18	
24	23.16	5,050	12.466	.08189	.005896	15–28	26.44	37.19	101.8	.07283	5.269	65.24	61.35	Mean = 61.138
25	22.98	5,066	15.157	.06737	.006399	12–17	24.01	38.95	107.2	.07660	5.278	65.28	61.20	
26	23.20	4,572	7.875	.12980	.004324	33–40	33.07	24.33	124.4	.08892	5.379	66.06	61.31	
27	23.18	4,570	9.408	.1085	.004730	23–29	30.23	25.37	130.4	.09330	5.381	66.16	61.18	
28	23.00	5,145	84.270	.1211	.01595	1–4	4.69	75.83	130.3	.09322	5.379	66.14	61.16	
29	22.99	5,073	23.223	.04393	.008488	6–12	19.06	33.47	156.8	.1117	5.529	67.36	61.37	

No.	Tem. ° C.	P.D. (Volts).	t_g (Sec.).	V_1 cm./sec.	$(V_1+V_2)_0$	n	$a\times10^5$ cm.	p (cm. Hg).	$1/pa$	l/a	$e_1\times10^{10}$	$e_1^{\frac{2}{3}}\times10^8$	$e^{\frac{2}{3}}\times10^8$	
30	23.19	5,090	26.830	.03801	.009111	5–10	17.77	35.18	160.2	.1147	5.507	67.18	61.06	Mean = 61.138
31	22.89	5,098	38.479	.02649	.011180	3–5	14.71	36.51	176.5	.1263	5.621	68.12	61.38	
32	23.06	5,070	14.060	.07246	.006762	12–17	24.29	21.12	195.0	.1394	5.692	68.67	61.22	
33	23.07	4,582	18.229	.05601	.006981	10–13	21.33	23.86	196.6	.1405	5.687	68.64	61.13	
34	23.06	5,061	38.010	.02682	.011205	3–8	14.72	34.01	199.8	.1429	5.714	68.84	61.20	
35	23.00	4,246	9.265	.11032	.004653	27–34	29.84	16.00	209.5	.1499	5.739	69.07	61.07	
36	22.91	4,236	9.879	.10340	.004863	24–28	28.74	15.67	222.0	.1589	5.820	69.71	61.23	
37	23.06	4,236	12.040	.08496	.005362	18–24	26.27	16.75	227.5	.1625	5.821	69.72	61.03	
38	22.94	2,556	10.657	.09581	.003109	32–43	27.49	14.70	247.5	.1771	5.935	70.61	61.16	
39	23.00	5,054	19.950	.05115	.008370	8–15	20.12	19.73	251.8	.1802	5.910	70.41	60.79	
40	23.09	5,058	21.130	.04830	.008865	7–9	18.38	18.54	278.3	.1993	6.076	71.72	61.09	
41	23.05	5,062	24.008	.04254	.009496	6–8	18.16	19.01	289.6	.2073	6.110	72.03	60.97	
42	22.94	4,238	18.347	.05564	.007110	9–17	20.60	15.72	308.8	.2210	6.224	73.04	61.24	
43	23.18	3,254	13.909	.07340	.004729	16–28	23.70	13.55	311.0	.2227	6.214	72.83	60.95	
44	23.04	4,231	29.114	.03503	.009273	5–9	16.16	17.17	360.6	.2579	6.466	74.77	61.00	
45	22.97	3,317	29.776	.03425	.007430	5–12	15.90	17.27	364.2	.2606	6.537	75.30	61.39	
46	22.81	3,401	25.909	.03937	.007311	6–19	16.90	14.68	403.3	.2886	6.719	76.71	61.30	
47	22.83	2,550	12.891	.07921	.003935	18–42	23.80	9.70	432.8	.3097	6.841	77.66	61.13	
48	22.80	2,559	32.326	.03150	.006286	7–14	15.01	15.35	433.8	.3104	6.866	77.85	61.28	
49	23.02	3,370	14.983	.06815	.011353	8–9	22.00	10.10	448.8	.3221	6.936	78.36	61.22	
50	23.45	2,535	11.659	.08757	.003783	25–30	24.88	8.60	466.7	.3340	6.978	78.67	60.85	
51	23.48	2,539	10.924	.09346	.003615	27–34	25.69	8.26	470.7	.3368	7.024	79.02	61.04	
52	22.98	3,351	50.400	.02021	.010775	2–6	11.83	16.95	498.5	.3568	7.210	80.40	61.36	
53	23.16	2,451	33.379	.03055	.006623	5–10	14.39	12.61	551.3	.3945	7.470	82.19	61.13	
54	23.46	2,533	19.227	.05347	.005314	11–17	18.87	9.03	587.8	.4112	7.661	83.73	61.18	
55	22.90	2,546	24.254	.04206	.006041	9–18	16.72	10.11	591.5	.4233	7.672	83.82	61.22	
56	23.21	1,700	5.058	.20256	.001861	117–136	36.53	4.46	614.2	.4396	7.777	84.57	61.11	
57	23.12	2,321	15.473	.06599	.004360	18–24	20.85	7.74	619.7	.4435	7.774	84.54	60.87	
58	23.03	3,388.5	24.33	.04196	.008183	6–10	16.62	9.070	620.2	.4439	7.810	84.83	61.14	

Mean of all numbers in last column = 61.138
Mean of first 23 numbers = 61.120


$e_1^{2/3} \times 10^8$
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$\frac{1}{pa}$
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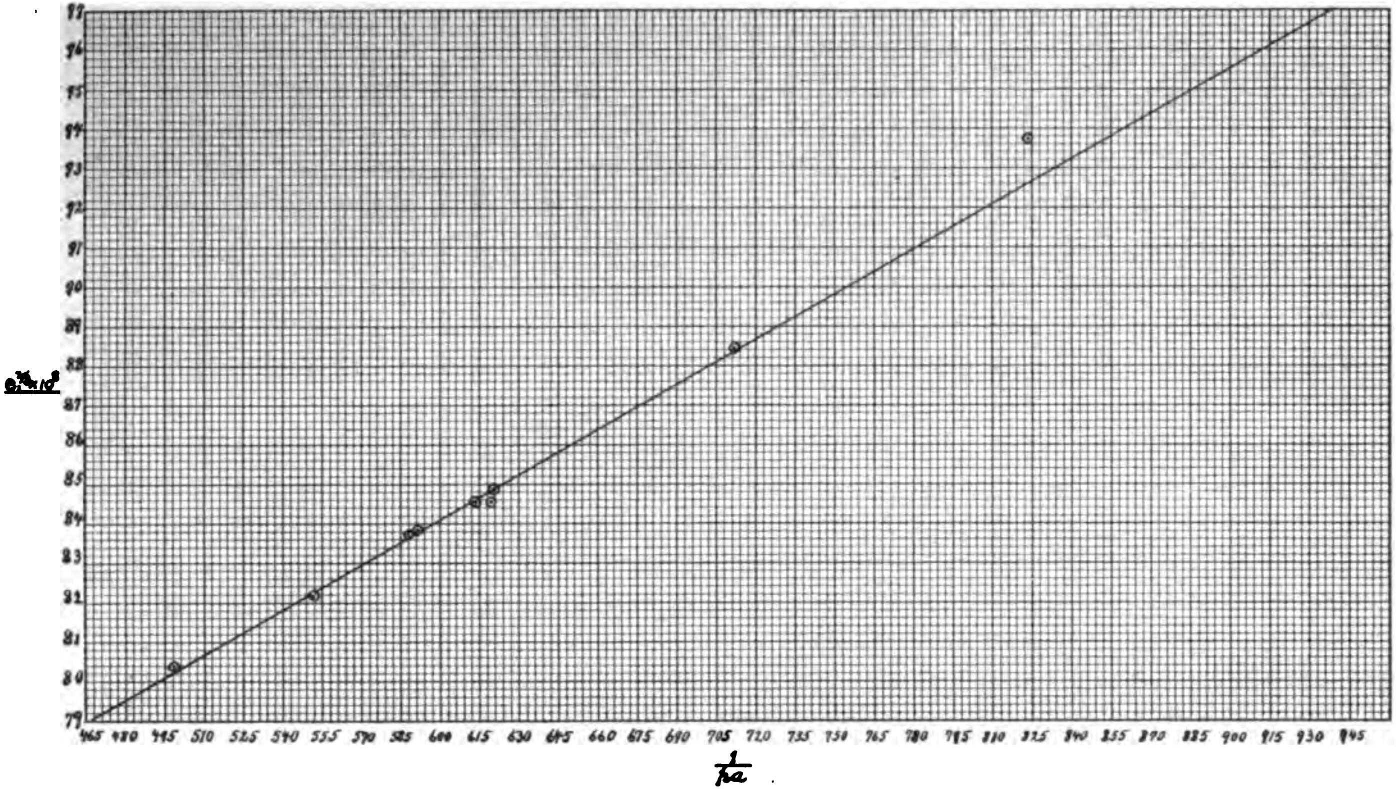
480

Fig. 2.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630
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660
675
690
705
720
735
750
765
780
795
810
825
840
855
870
885
900
915
930
945
$\frac{1}{pa}$

Fig. 3.

y intercept (see equation 9). In view of the uncertainty in l due to the fact that k in the equation $\eta = knm\bar{c}l$ has never been exactly evaluated, it was thought preferable to write the correction term to Stokes's law (see (2 and 3) in the form $(1 + b/pa)^{-1}$ instead of in the form $(1 + Al/a)^{-1}$ and then to plot $e_1^{\frac{2}{3}}$ against $1/pa$. Nevertheless in view of the greater ease of visualization of l/a all the values of this quantity corresponding to successive values of $1/pa$ are given in Table XX., k being taken, merely for the purposes of this computation, as .3502 (Boltzmann). Fig. 2 shows the graph obtained by plotting the values of $e_1^{\frac{2}{3}}$ against $1/pa$ for the first 51 drops of Table XX., and Fig. 3 shows the extension of this graph to twice as large values of $1/pa$ and $e_1^{\frac{2}{3}}$. It will be seen that there is not the slightest indication of a departure from a linear relation between $e_1^{\frac{2}{3}}$ and $1/pa$ up to the value $1/pa = 620.2$ which corresponds to a value of l/a of .4439 (see drop No. 58, Table XX.). Furthermore the scale used in the plotting is such that a point which is one division above or below the line in Fig. 2 represents in the mean an error of 2 in 700. *It will be seen from Figs. 2 and 3 that there is but one drop in the 58 whose departure from the line amounts to as much as 0.5 per cent. It is to be remarked, too, that this is not a selected group of drops but represents all of the drops experimented upon during 60 consecutive days,* during which time the apparatus was taken down several times and set up anew. It is certain then that an equation of the form (2) holds very accurately up to $l/a = .4$. The last drop in Fig. 3 seems to indicate the beginning of a departure from this linear relationship. Since such departure has no bearing upon the evaluation of e, discussion of it wil be postponed to another paper.

Attention may also be called to the completeness of the answers furnished by Figs. 2 and 3 to the questions raised in § 6. Thus drops No. 27 and 28 have practically identical values of $1/pa$ but while No. 28 carries, during part of the time, but 1 unit of charge (see Table XX.) drop No. 27 carries 29 times as much and it has about 7 times as large a diameter. Now if the small drop were denser than the large one (see assumption 3, § 6) or if the drag of the median upon the heavily charged drop were greater than its drag upon the one lightly charged (see assumtion 1, § 6), then for both these reasons drop 27 would move more slowly relatively to drop 28 then would otherwise be the case and hence $e_1^{\frac{2}{3}}$ for 27 would fall below $e_1^{\frac{2}{3}}$ for drop 28. Instead of this the two $e_1^{\frac{2}{3}}$'s fall so nearly together that it is impossible to represent them on the present scale by two separate dots. Drops 52 and 56 furnish an even more striking confirmation of the same conclusion, for both drops have about the same value for l/a and both are exactly on the line though No. 56

carries at one time 68 times as heavy a charge as No. 52 and has three times as large a radius. In general the fact that Figs. 2 and 3 show no tendency whatever on the part of either the very small or the very large drops to fall above or below the line is experimental proof of the joint correctness of assumptions 1, 3, and 2*b* of § 6. The correctness of 2*a* was shown by the agreement throughout Tables IV. to XIX. between $1/n'(1/t_F' - 1/t_F)$ and $1/n(1/t_g + 1/t_F)$.

The values of $e^{\frac{2}{3}}$ and b obtained graphically from the y-intercept and the slope in Fig. 2 are $e^{\frac{2}{3}} = 61.13 \times 10^{-8}$ and $b = .0006254$, p being measured, for the purposes of Fig. 2 and of this computation in mm. of Hg at 23° C. and a being measured in cm. The value of A (equations 2 and 3) corresponding to this value of B is *.874* instead of .817 as originally found. Cunningham's theory gives, in terms of the constants here used, $A = 788$.[1]

Instead however of taking the result of this graphical evaluation of $e^{\frac{2}{3}}$ it is more accurate to reduce each of the observations on $e_1^{\frac{2}{3}}$ to $e^{\frac{2}{3}}$ by means of the above value of B and the equation

$$e^{\frac{2}{3}}\left(1 + \frac{b}{pa}\right) = e_1^{\frac{2}{3}}. \tag{14}$$

The results of this reduction are contained in the last column of Table XX. These results illustrate very clearly the sort of consistency obtained in these observations. *The largest departure from the mean value found anywhere in the table amounts to 0.5 per cent., and "the probable error" of the final mean value computed in the usual way is 16 in 61,000.*

Instead however of using this final mean value as the most reliable evaluation of $e^{\frac{2}{3}}$ it was thought preferable to make a considerable number of observations at atmospheric pressure on drops small enough to make t_g determinable with great accuracy and yet large enough so that the whole correction term to Stokes's law amounted to but a few per cent., since in this case, even, though there might be a considerable error in the correction-term constant b, such error would influence the final value of e by an inappreciable amount. The first 23 drops of Table XX. represent such observations. It will be seen that they show slightly greater consistency than do the remaining drops in the table and that the correction-term reductions for these drops all lie between 1.3 per cent. (drop No. 1) and 5.6 per cent. (drop No. 23) so that even though b were in error by as much as 3 per cent. (its error is actually not more than .5 per cent.) $e^{\frac{2}{3}}$ would be influenced by that fact to the extent of but 0.1 per cent. The mean value of $e^{\frac{2}{3}}$ obtained from the first 23 drops is 61.12×10^{-8}, a number which differs by 1 part in 3,400 from the mean obtained from all the drops.

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[1] Phys. Rev., 32, p. 380; also footnote.

When correction is made for the fact that the numbers in Table XX. were obtained on the basis of the assumption $\eta_{23} = .0001825$, instead of $\eta_{23} = .0001824$ (see § 2) the final mean value of $e^{\frac{2}{3}}$ obtained from the first 23 drops is 61.085×10^{-8}. This corresponds to

$$e = 4.774 \times 10^{-10} \text{ electrostatic units.}$$

Since the value of the Faraday constant has now been fixed virtually by international agreement[1] at 9,650 absolute electromagnetic units and since this is the number N of molecules in a gram molecule times the elementary electrical charge, we have

$$N \times 4.774 \times 10^{-10} = 9{,}650 \times 2.9990 \times 10^{10};$$

$$\therefore \quad N = 6.062 \times 10^{23}.$$

Although the probable error in this number computed by the method of least squares from Table XX. is but one part in 3,000 it would be erroneous to infer that e and N are now known with that degree of precision, for there are four constant factors entering into all of the results in Table XX. and introducing uncertainties as follows. The coefficient of viscosity η which appears in the 3/2 power introduces into e and N a maximum possible uncertainty of 0.1 per cent. The distance between the condenser plates (16.00 mm.) is correct to .01 mm., and therefore, since it appears in the 1st power in e, introduces a maximum possible error of something less than 0.1 per cent. The voltmeter readings have a maximum possible error of rather less than 0.1 per cent., and carry this in the 1st power into e and N. The cross-hair distance which is uniformly duplicatable to one part in a thousand appears in the 3/2 power and introduces an uncertainty of no more than 0.1 per cent. The other factors introduce errors which are negligible in comparison. *The uncertainty in e and N is then that due to 4 continuous factors each of which introduces a maximum possible uncertainty of 0.1 per cent.* Following the usual procedure we may estimate the uncertainty in e and N as the square root of the sum of the squares of these four uncertainties, that is, as 2 parts in 1,000. We have then finally:

$$\mathbf{e} = 4.774 \pm .009 \times 10^{-10}$$

and

$$\mathbf{N} = 6.062 \pm .012 \times 10^{23}.$$

The difference between these numbers and those originally found by the oil-drop method, viz., $e = 4.891$ and $N = 5.992$ is due to the fact that this much more elaborate and prolonged study has had the effect of changing every one of the three factors η, A, and d (= cross-hair distance) in such a way as to lower e and to raise N. The chief change however has been due to the elimination of the faults of the original optical system.

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[1] Atomic weight of silver 107.88. Electrochemical equivalent of silver 0.01118.

11. Comparison with Other Measurements.

So far as I am aware, there is at present no determination of e or N by any other method which does not involve an uncertainty at least 15 times as great as that represented in the above measurements.

Thus the *radioactive method* yields in the hands of Regener[1] a count of the α particles which gives e with an uncertainty which he estimates at 3 per cent. This is as high a precision I think as has yet been claimed for any α particle count,[2] though Geiger and Rutherford's photographic registration[3] method will doubtless be able to improve it.

The *Brownian Movement* method yields results which fluctuate between Perrin's value[4] $e = 4.24 \times 10^{-10}$, and Fletcher's value,[5] 5.01×10^{-10}, with Svedberg's measurements[6] yielding the intermediate number 4.7×10^{-10}.

The *radiation method* of Planck[7] yields N as a product of $(c_2)^3$ and σ. The latest Reichsanstalt value of c_2 is 1.436[8] while Coblentz,[9] as the result of extraordinarily careful and prolonged measurements obtains 1.4456. The difference in these two values of $(c_2)^3$ is 2 per cent. Westphal[10] estimates his error in the measurement of σ at .5 per cent. though reliable observers differ in it by 5 per cent. or 6 per cent. We may take then 3 per cent. as the limit of accuracy thus far attained in measurements of e or N by other methods. *The mean results by each one of the three other methods fall well within this limit of the value found above by the oil-drop method.*

12. Computation of Other Fundamental Constants.

For the sake of comparison and reference, the following fundamental constants are recomputed on the basis of the above measurements:

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[1] Regener, Sitz. Ber. d. k. Preuss. Acad., 37, p. 948, 1909.

[2] Rutherford and Geiger, Proc. Roy. Soc., 81, p. 155, 1908.

[3] Geiger and Rutherford, Phil. Mag., 24, p. 618, 1912.

[4] J. Perrin, C. R., 152, p. 1165, 1911.

[5] H. Fletcher, Phys. Rev., 33, p. 107, 1911.

[6] Svedberg, Arkiv f. Kemi, etc., utg. af K. Sv. Vetensk. Akad., 2, 29, 1906. See also Svedberg, "Die Existenz der Mölekule," p. 136. Leipzig, 1912.

[7] Planck, Vorlesungen über die Theorie der Wärmestrahlung, 2d edition, 1913, p. 166.

[8] See Planck, Vorles., p. 163.

[9] Coblentz, Journal of the Washington Academy of Sciences, Vol. 3, p. 178, April, 1913.

[10] Wm. H. Westphal, Verh. d. D. Phys. Ges., 13, p. 987, Dec., 1912.

1. The number n of molecules in 1 c.c. of an ideal gas at 0° 76 is given by

$$n = \frac{N}{V} = \frac{6.062 \times 10^{23}}{22,412} = 2.705 \times 10^{19}.$$

2. The mean kinetic energy of agitation E_0 of a molecule at 0° C. is given by

$$pV = \tfrac{1}{3}Nmu^2 = \tfrac{2}{3}NE_0 = RT,$$

$$\therefore\ E_0 = \frac{3}{2}\frac{p_0V_0}{N} = \frac{3 \times 1,013,700 \times 22,412}{2 \times 6.062 \times 10^{23}} = 5.621 \times 10^{-14} \text{ ergs.}$$

3. The constant ϵ of molecular energy defined by $E_0 = \epsilon T$ is given by

$$\epsilon = \frac{E_0}{T} = \frac{5.621 \times 10^{-14}}{273.11} = 2.058 \times 10^{-16} \frac{\text{ergs}}{\text{degrees}}.$$

4. The Boltzmann entropy constant k defined by $S = k \log W$ is given by[1]

$$k = \frac{R}{N} = \frac{p_0V_0}{TN} = \tfrac{2}{3}\epsilon = 1.372 \times 10^{-16} \frac{\text{ergs}}{\text{degrees}}.$$

All of these constants are known with precisely the accuracy attained in the measurement of e.

5. The Planck "Wirkungsquantum" h can probably be obtained considerably more accurately as follows than in any other way. From equation 292, p. 166, of the "Wärmestrahlung," we obtain[2]

$$h = \frac{k^{4/3}}{c}\left(\frac{48\pi\alpha}{a}\right)^{1/3} = \frac{(1.372 \times 10^{-16})^{4/3}}{2.999 \times 10^{10}} \cdot \left(\frac{48\pi 1.0823}{7.39 \times 10^{-15}}\right)^{1/3} = 6.620 \times 10^{-27}$$

which gives h with the same accuracy attainable in the measurement of $k^{4/3}/a$ in which a is the Stefan-Boltzmann constant. If Westphal's estimate of his error in the measurement of this constant is correct, viz., 0.5 per cent., it would introduce an uncertainty of but 0.2 per cent. into h. This is about that introduced by the above determination of $k^{4/3}$, hence the above value of h should not be in error by more than 0.4 per cent.

6. The constant c_2 of the Wien-Planck radiation law may also be computed with much precision from the above measurements. For also from equation 292 of the "Wärmestrahlung" we obtain

$$c_2 = \left(\frac{48\pi\alpha k}{a}\right)^{1/3} = \left(\frac{48\pi 1.0823\ 1.372 \times 10^{-16}}{7.39 \times 10^{-15}}\right)^{1/3} = 1.4470 \text{ cm. degrees.}$$

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[1] See Planck's Vorles., p. 129.

[2] c = velocity of light, α = a numerical factor, and $a = 4\sigma/c$. Westphal's value of σ is 5.54×10^{-6} which corresponds to $a = 7.39 \times 10^{-15}$.

Since both k and a here appear in the 1/3 power, the error in c should be no more than 0.2 per cent., provided Westphal's error is no more than 0.5 per cent.

The difference between this and Coblentz's mean value, viz., *1.4456* is but 0.1 per cent. The agreement is then entirely satisfactory. A further independent check is found in the fact that Day and Sosman's location of the melting point of platinum at 1755° C.[1] is equivalent to a value of $c_2 = 1.4475$.[2] On the other hand, the last Reichsanstalt value of c_2, viz., 1.437, is too low to fit well with these and Westphal's measurements. It fits perfectly however with a combination of the above value of e and Shakespear's[3] value of σ, viz., $\sigma = 5.67 \times 10^{-5}$.

13. SUMMARY.

The results of this work may be summarized in the following table in which the numbers in the error column represent in the case of the first six numbers estimated limits of uncertainty rather than the so-called "probable errors" which would be much smaller. The last two constants however involve Westphal's measurements and estimates and Planck's equations as well as my own observations.

TABLE XXI.

Elementary electrical charge	$e = 4.774 \pm .009 \times 10^{-10}$
Number of molecules per gram molecule	$N = 6.062 \pm .012 \times 10^{23}$
Number of gas molecules per c.c. at 0° 76	$n = 2.705 \pm .005 \times 10^{19}$
Kinetic energy of a molecule at 0° C	$E_0 = 5.621 \pm .010 \times 10^{-14}$
Constant of molecular energy	$\epsilon = 2.058 \pm .004 \times 10^{-16}$
Constant of the entropy equation	$k = 1.372 \pm .002 \times 10^{-16}$
Elementary "Wirkungsquantum"	$h = 6.620 \pm .025 \times 10^{-27}$
Constant of the Wien displacement law	$c_2 = 1.4470 \pm 0030$

I take pleasure in acknowledging the able assistance of Mr. J. Yinbong Lee in making some of the above observations. Mr. Lee has also repeated with my apparatus the observations on oil at atmospheric pressure with results which are nearly as consistent as the above. Using my value of b he obtains, as a mean of measurements on 14 drops, a value of e which differs from the above by less than 1 part in 6,000, although its probable error computed as in the case of Table XX. is 1 part in 2,000.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
June 2, 1913.

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[1] Amer. Jour. Sci., 30, p. 3, 1910.

[2] Coblentz, Journal of the Washington Academy of Sciences, Vol. 3, p. 13.

[3] G. A. Shakespear, Proc. Roy. Soc., 86, 180, 1911.

THE EMISSIVITY OF OXIDIZED METALLIC SURFACES.[1]

BY C. P. RANDOLPH AND M. J. OVERHOLSER.

THE measurements here described were undertaken to secure data on the total radiation from oxidized metallic surfaces, at temperatures below 700° C. Total radiation includes all the energy dissipated from a surface by radiation, at wave-lengths from 0 to ∞. A large amount of accurate work on selective radiation is available, but comparatively little on total radiation. Data on the latter are necessary when dealing with heat losses from surfaces.

The emissivity of a body is here defined as the ratio of the energy radiated by a body of emissivity e, to the energy radiated by a black body, when both are at the same temperature. This is not the definition always used,[2] but it is the most convenient for comparing different surfaces when dealing with total radiation.[3] A "black body" is, of course, one that absorbs all the radiation incident upon it, no matter what the wave-length. From the Stefan-Boltzman law, for a black body

$$W = \sigma(T_1^4 - T_2^4),$$

where W is the rate of heat loss, σ is a constant experimentally determined, and T_1 and T_2 are the absolute temperatures respectively of the radiating surface and of the surroundings. Then for a body of emissivity e,

$$W = e\sigma(T_1^4 - T_2^4).$$

The construction of the apparatus used for comparing the radiation from various surfaces with that from a black body is shown in Figs. 1 and 2. It was our aim to construct a robust instrument that could be used in connection with a Leeds and Northrup potentiometer (read accurately to .001 millivolt), thus making it unnecessary to observe galvanometer deflections. Of course there are many radiometers far more delicate than this.

The absorbing disc A (Fig. 1) is of platinum .25 mm. thick, coated with platinum-black on the side presented to the radiating surface. It is supported by three wires (one is shown at K), .25 mm. diameter, and

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[1] From the heating device research laboratory, General Electric Company.

[2] Preston's Theory of Heat, 2d ed., 587.

[3] Poynting and Thompson's Heat, 233.

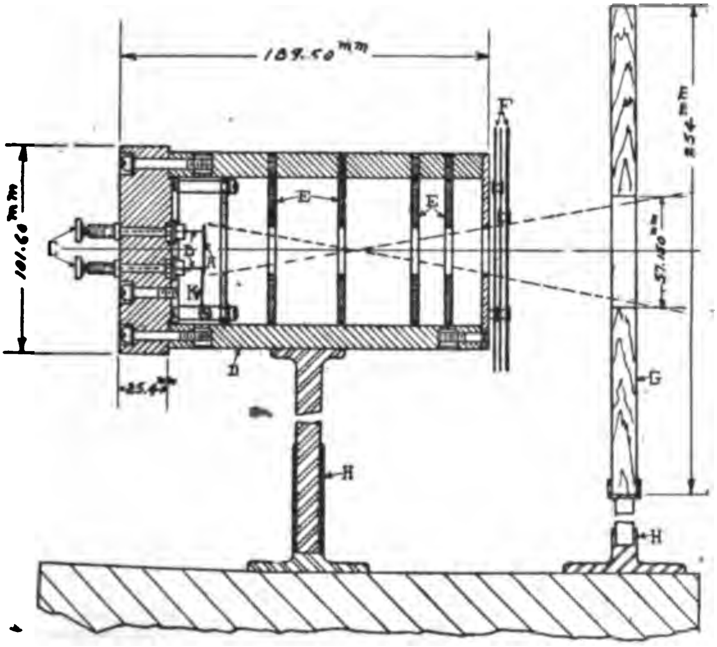

Fig. 1.

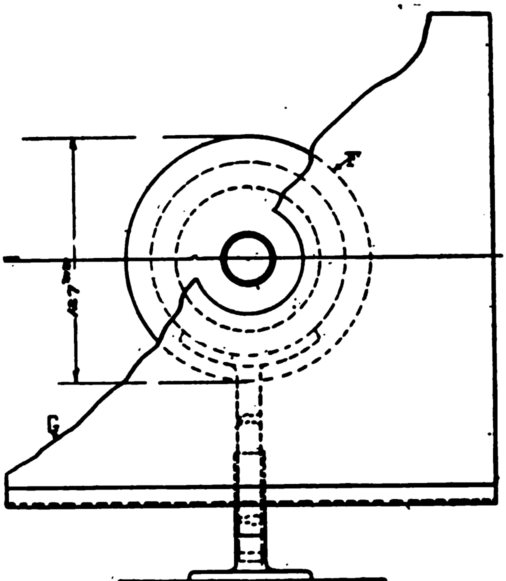

Fig. 2.

to the disc is soldered (on the polished side) a bismuth-iron thermo-couple *B*. The cold junctions of the thermo-couple are brought out to the binding posts *C*, which are always at room temperature. The walls *D* are of hard rubber, so thick that they can heat very slightly in the short time the instrument is exposed to a radiating surface for a measurement. Baffles *EE*, also of black hard rubber, prevent any heating of the absorber *A* by convection, and also prevent reflection of radiant heat from the walls *D* to the absorber. Three thin brass discs *F* protect the end wall *G* from being heated by the radiating surface. It was found necessary also to protect the side walls from radiation by placing a square wooden shield *G* between the radiometer and the radiating surface. This shield is somewhat larger than any of the radiating surfaces used in the measurements, and is painted black on the side away from the radiometer to reduce reflection to a minimum. The cylinder *D* and the shield *G* are supported by brass rods fitting in tubes *HH* and can be adjusted at any height with thumb screws.

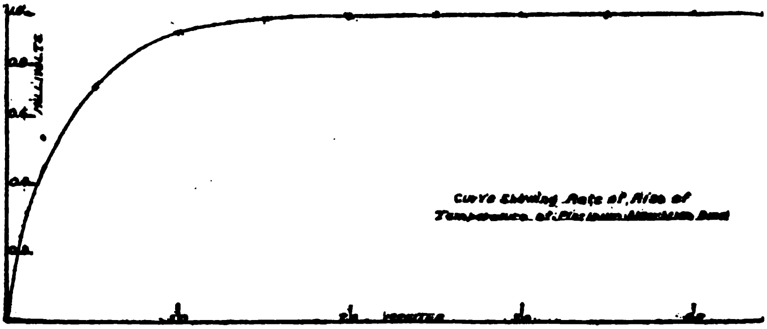

Fig. 3.

The curve in Fig. 3 for the rate of rise of temperature of the platinum absorber shows that it reaches a maximum temperature three minutes after exposure. All readings were taken after an exposure of four minutes, to make sure that the horizontal part of the curve had been reached. No lenses or reflectors are used in the design of the radiometer, and therefore the only chance of error from selective absorption is that the platinum absorber itself might possess this property. But platinum-black comes very close to being a black body, so that the possibility of error here is very slight.

The radiation through a relatively small opening in a closed uniform temperature surface has been shown to be black-body radiation, no matter what the material of the surface may be.[1] This fact was made use of in calibrating the radiometer. Fig. 4 shows the "black body." *A* is a large cast-iron pipe, closed at the rear with another heavy casting *B*. The pipe and the casting *B* are heated by three "calorite" wire resistors *CC* so connected that the energy dissipated by each heating unit can be adjusted independently. The temperature is thus kept very uniform. Five thermo-couples *DD* were used for measuring the temperature, which could be kept uniform within 3° C. at 500° C. The iron castings were surrounded with insulation, as shown, which reduces the energy necessary for maintaining any temperature, and makes it easier to maintain a uniform temperature. A water jacket *E* prevents the outher wall from heating at the end. The baffles *FF* make the inner surface approximate more closely to an entirely closed surface, thus reducing to a minimum the difference between the radiation from the casting and that from a perfectly black body.

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[1] Balfour Stewart, Lessons in Elementary Physics.

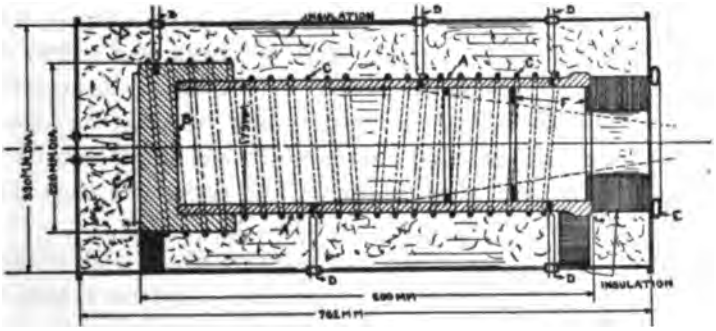

Fig. 4.

The rate at which energy was radiated from the black body was calculated from its observed temperatures and the temperature of the surroundings, by substituting in the Stefan-Boltzman equation. A calibration curve was plotted for the radiometer showing the relation between millivolts and energy radiated. The temperature of the surroundings was taken as 25° C., in all measurements. Where the radiating surface is at a temperature above about 175° C., a change in the room temperature of a few degrees can easily be shown to introduce only a negligible error.

Since

$$e = \frac{e\sigma(T_1^4 - T_2^4)}{\sigma(T_1^4 - T_2^4)}$$

the value of σ does not affect the results and temperature errors also correct themselves to a certain extent. The platinum-platinum-iridium thermo-couples used for measuring the temperatures of the black body and of the oxidized surfaces were calibrated under exactly the same conditions.

A metal disc 19.1 cm. diameter and 6 mm. to 13 mm. thick, mounted vertically, with its exposed surface flush with the end of a horizontal iron cylinder (the axis of the disc and the cylinder coinciding) formed the radiating surface of which the emissivities were measured.[1] The heating unit was made of a calorite resistance ribbon between two mica discs. This unit was clamped between the radiating disc and a thin disc of sheet steel. The cylinder back of the 19 cm. disc was filled with good heat insulating material, thus decreasing the energy necessary to maintain the radiating disc at any temperature. The thermo-couple was held firmly against the back of the disc under the head of a screw, the two leads being brought out to the cold junction (kept in oil) through the heat insulation. There was a space of about 19 mm. between the edges of the disc and the inside of the cylinder walls which was also filled with insulation, held in place with a mica ring. The surface of each disc was cleaned and polished before it was mounted.

The thermo-couple measures the temperature of the back of the metal disc and not that of the radiating surface itself. In some cases—as with copper and other good heat conductors—this drop in temperature between the two surfaces of the disc is negligible. With poor heat conductors—as certain alloys—it is very important to make a correction at higher temperatures. We had previously accurately measured the thermal conductivity at various temperatures of nearly all the metals or alloys used in these experiments, and for those which we had not measured ourselves the values were obtained from the literature.[2] The wattmeter readings gave the total energy required to maintain a surface at any temperature. The watts per square centimeter lost from the surfaces by radiation and convection was calculated by subtracting the heat conducted through the insulation, from the wattmeter reading. Then the actual temperature of the radiating surface is

$$T_1 = t - WRL,$$

where t is the temperature as measured with the thermo-couple, W is the heat flux through the metal disc, R is the thermal resistivity of the metal and L is the thickness of the plate. As this correction is in all cases relatively small, any possible error in it becomes negligible in the final results. With the type of heating unit used, the thickness of the plate was always made great enough to insure a very uniform temperature over its surface.

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[1] The method of mounting the metal plate is fully described with drawings by I. Langmuir in J. Am. Elec. Soc., XXIII., 14 (1913).

[2] Jaeger and Disselhorst, Wiss. Abh. d. Phys. Techn. Reichanst., 3, 269 (1900); Angell, PHYS. REV., XXXIII., 421 (1911).

We found on beginning the measurements given below that the emis-

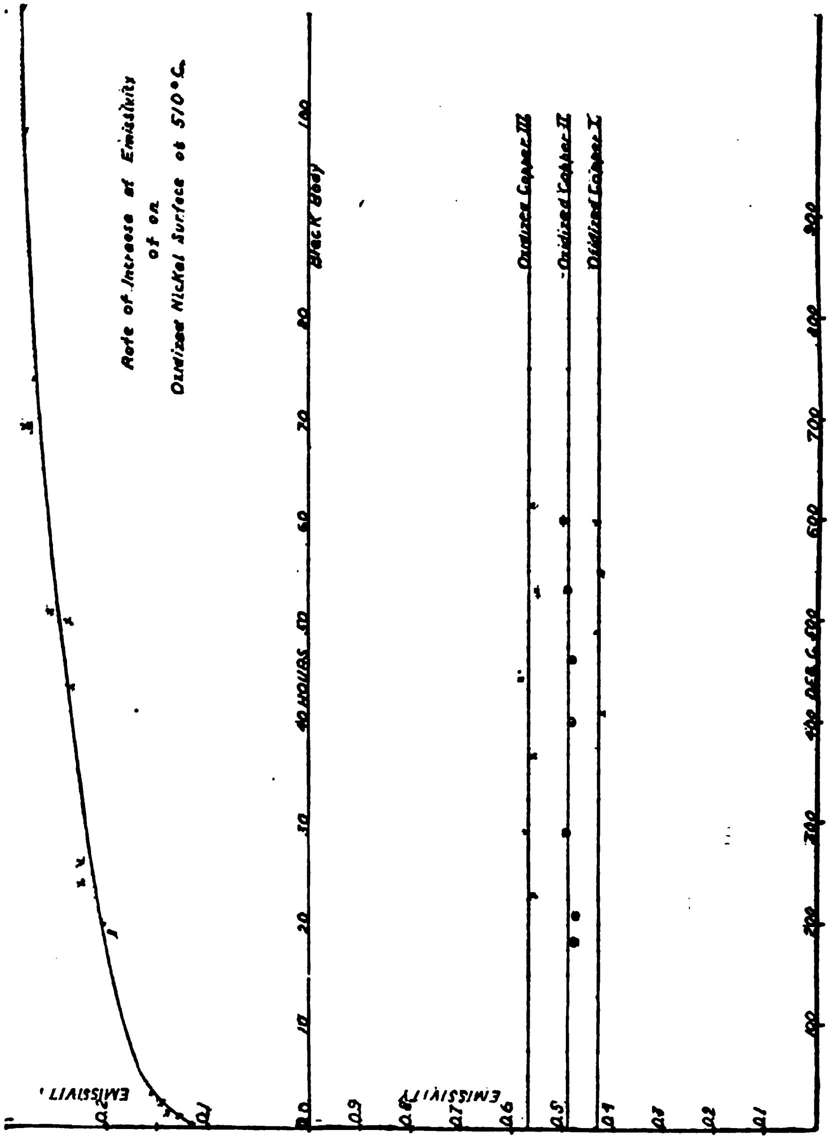

Fig. 5.

sivity increases (1) with the temperature to which the surface has pre-
sivity of a surface depends on the depth of oxidation; that is, the emis-

viously been heated and (2) with the time the surface is kept at any temperature. In Fig. 5 is shown the rate of increase of the emissivity of an oxidized nickel surface at 510° C. Zero time is here taken as the time when we could get the first measurement after the surface had been quickly heated to 510° C., starting with a polished surface. The constant value is seen to be .283. The temperature was then increased to 583°, where the constant value of the emissivity was .410. In Fig. 6 it is seen that the maximum emissivity is .49, when the surface is heated to 640° C. With the exception of the oxidized copper surface, in all the measurements made, the method was to start with a polished surface which was kept at the maximum temperature for which a point is given on the curves, until the emissivity had become constant. Measurements were then taken at various lower temperatures.

Fig. 5 shows a series of measurements at different temperatures for oxidized copper. Curves I. and II. were determined by measuring the emissivity before it had become constant at the maximum temperatures for which results are given. Then observations were taken at various lower temperatures as explained above. Curve III. was obtained in the usual way, by heating the surface at the maximum temperature until the radiation was constant. It is seen that if a copper surface is heated for even a *very short time* at a temperature A about 50° higher than temperature B, the emissivity has reached or passed the maximum value it would attain if the surface had been kept at B indefinitely.

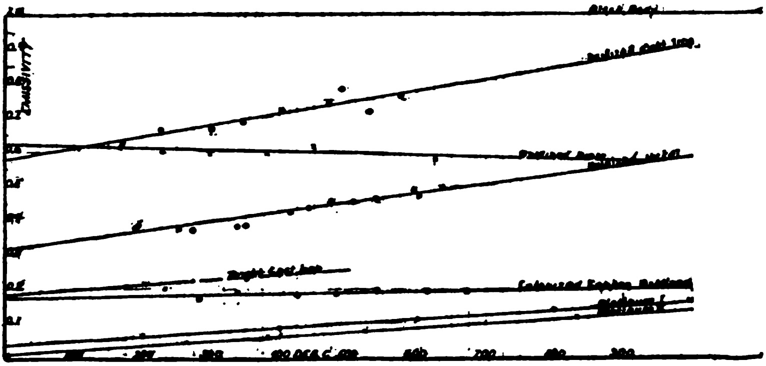

Fig. 6.

The curves for calorized copper and calorized steel (Figs. 6 and 7) refer to plates of the above metals which have been impregnated with aluminum in their surfaces. This process requires that they be heated to a temperature above that at which measurements were made, so that we would expect no variation of emissivity with time of heating. This agrees with the experimental results.

The emissivities of platinum and silver (Figs. 6 and 7) are taken from the literature, and are given here for comparison. The values for silver and platinum I. are calculated from Hagen and Ruben's formula[1] for long wave-length radiation:

$$e = .365\frac{r}{\lambda},$$

where e = emissivity,

r = electrical resistivity in ohms per cm^3,

λ = wave-length of radiant energy in cm.

λ is determined by Wien's law, which gives the relation between the absolute temperature T and the wave-length of maximum intensity, viz.,

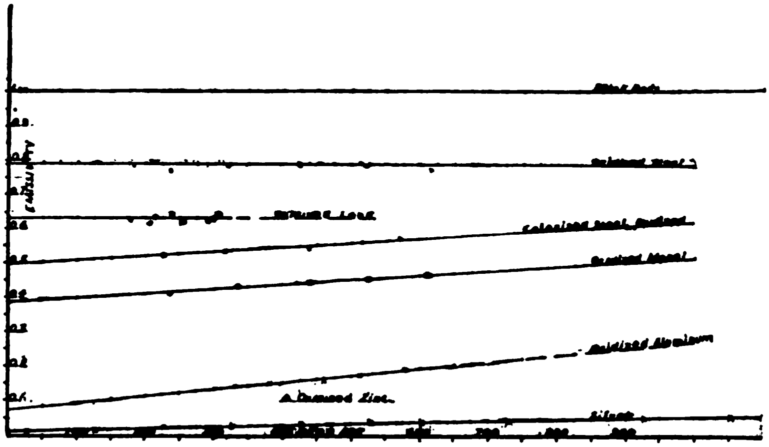

Fig. 7.

$$\lambda_m = \frac{.290}{T}\text{ cm}.$$

For the sample of silver for which the emissivity is here calculated, $r = 1.76 \times 10^{-6}$ at 0° C. Jaeger and Disselhorst[2] found the temperature coefficient of the electrical resistivity of silver to be .0040. Therefore

$$e = .61 \times 10^{-3}\sqrt{T(1+.0040T)}.$$

Platinum I. is a sample used by I. Langmuir in measuring convection losses.[3] He measured the electrical resistivity at various temperatures, and the emissivity is calculated from these results as for silver. The curve platinum II. is taken from actual measurements of emissivity by Lummer and Kurlbaum.[1]

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[1] Hagen and Ruben's Ann. Phys., 8, 1 (1902).

[2] Jaeger and Disselhorst, Phys. Tech. Reich., 3, 269 (1900).

[3] I. Langmuir, Phys. Rev., XXXIV., 401 (1912).

The values of emissivities in the following table are taken from the curves and are given here for convenience.

	Temperature, Deg. C.		
	200	400	600
Silver	.020	.030	.038
Platinum (1)	.060	.086	.110
Oxidized zinc	——	.110	——
Oxidized aluminum	.113	.153	.192
Calorized copper, oxidized	.180	.185	.190
Cast iron	.210	——	——
Oxidized nickel	.369	.424	.478
Oxidized monel	.411	.439	.463
Calorized steel, oxidized	.521	.547	.570
Oxidized copper	.568	.568	.568
Oxidized brass	.610	.600	.589
Oxidized lead	.631	——	——
Oxidized cast iron	.643	.710	.777
Oxidized steel	.790	.788	.787
Black body	1.00	1.00	1.00

CONCLUSIONS.

1. The emissivity of an oxidized metallic surface depends on the depth of the surface oxidation. Therefore it is a function (*a*) of the temperature to which the surface has previously been heated and (*b*) of the time the surface has been maintained at the temperature.

2. The emissivities of certain surfaces have been measured at various temperatures and the results are given here. The surfaces were oxidized at about 600° (the temperature of oxidation is always the highest shown on the temperature-emissivity curves) until the emissivity had become constant.

3. It is possible that the variations so often found in scientific literature in measurements of heat losses from surfaces are due to changes in the radiation and not to unsteady convection losses.

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[1] Lummer and Kurlbaum, Verh. Phys., Ges., Berlin, 17, 106 (1898).

THE ACTION OF MERCURY VAPOR ON SELENIUM.

By F. C. Brown.

PREVIOUSLY[1] I have shown that all the known changes of conductivity of selenium with the time of exposure to light can be explained mathematically by assuming a dynamic equilibrium between three components *A*, *B* and *C*. But in this analysis there appeared on obvious physical interpretation of the varying initial rates of change which were imposed on the different varieties of selenium for equilibrium in the dark. This fact has led the author to search for the conditions which will consistently and certainly produce one of the varieties of selenium about which there is most dispute, viz., light-negative selenium. The question as to whether the light-negative property is in the selenium itself or is in impurities, or selenium compounds, was one that had to be definitely settled. While the search has not answered all questions that have arisen, it has proved worth while in that it has resulted in some definite advances, that are interesting and which further limit future investigations. It is found that mercury vapor will uniformly transform different allotropic modifications of selenium into light-negative selenium, and further that the mercury vapor probably forms chemical union with the selenium.

In considering a relationship which I observed between the conductivity of selenium and its sensibility, viz., that light-negative selenium is associated with high conductivity, it occurred to me that any method that produces low resistance selenium might also at the same time produce light-negative selenium. In this connection it was noted that Moss[2] and later Minchin[3] had observed the remarkable decrease of resistance of selenium when it was placed in a vacuum produced by a mercury pump. Moss first exposed a bar of vitreous selenium to mercury vapor in a partial vacuum, whereupon he observed that the conductivity increased to a higher value than that of any known modification of selenium. He attributed this conductivity to a mercury film, and consequently it is not surprising that he overlooked the negative action of light. Minchin placed a light-positive selenium cell in a Sprengel vacuum. He observed that cells of several hundred thousand ohms decreased in resistance in three or four days to values as low as 50 ohms, but he did not observe any light sensitiveness after the low resistance was reached.

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[1] Phys. Rev., 33, pp. 1 and 403.

[2] Phil. Mag., Ser. 5, 3, p. 67, 1877.

[3] Nature, 77, p. 198 and p. 222, 1908.

THE CRYSTALLIZATION OF SELENIUM IN AN ATMOSPHERE IN WHICH MERCURY VAPOR IS PRESENT.

The first experiments that exhibited the action of mercury vapor on selenium were those in which the selenium in an ordinary cell form was crystallized in the presence of mercury vapor in air. The cell form consisted of two parallel wires wound around a porcelain cleat such as is used by the electrician for holding and insulating wires. The selenium was first melted on this cleat and then undercooled, thus giving the vitreous allotrope attached to the wires. This selenium form was then placed just over a heating bath of quartz sand. At the bottom of the sand was a globule of mercury. The bath was heated by a bunsen burner from below, and consequently the temperature of the mercury was much higher than that of the selenium. It was found that if the selenium was kept anywhere between 150° and 200°, its conductivity reached a very high value, which it maintained after cooling to room temperature. Immediately upon cooling the selenium displayed light-negative characteristics, *i. e.*, the conductivity decreased when the cell was illuminated.

It seems that the mercury diffused up through the sand and condensed on the selenium. As might be expected the higher the temperature of the sand bath and of the selenium, the sooner did the selenium reach an approximately constant high conductivity. If the selenium were kept at about 190° for about 10 minutes, the resistance of the cell would drop to about 20 ohms, while if the temperature were kept at 150° several hours were required in order that this conductivity might be attained. No differences in the light-characteristics could be detected by varying the temperatures within the range noted. However if the selenium were heated below 140° or above 200°, the light sensitiveness did not appear. Perhaps at the lower temperature an appreciable amount of the mercury vapor did not reach the selenium while at the higher temperatures an explanation must probably involve chemical union of the selenium and mercury or special allotropic modification of the selenium. Some thirty samples were made in this way, with but the use of a single drop of mercury in the sand bath.

The characteristics of the light-negative selenium prepared in this manner were not investigated fully, but many of them behaved much like the specimen described by Miss Crum.[1] Aside from the light-negative character, the irregularities and the lack of permanency were the most striking peculiarities. Frequently the resistance would take sudden jumps, particularly if the specimen was illuminated or jarred. Occasionally the selenium would be light-negative with faint illumination but light-positive with intense illumination, and even more frequently a specimen would temporarily change over from light-negative to light-positive character. At one time as many as one fourth of the samples in my possession were light-positive when tested with light of uniform intensity. Frequently the sensibility was quite great. One sample changed from 74.6 ohms in the dark to 104.0 ohms in the light. It maintained an average sensibility half as large for about a week. The irregularity of one sample is illustrated by the following readings taken with the selenium alternately in the dark and in the light, at intervals of about two minutes.

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[1] PHYS. REV., 33, 538, 1911.

Resistance in Dark.	Resistance in Light.
100	117
100	101.5
98.8	105.0
95	

Not all the samples made in this way were permanent. The maximum change of resistance by light was probably greatest about two days after manufacture. After that time the sensibility gradually decreased until finally after a month there was almost no effect due to light action.

It was considered possible so far as the above experiment decides that the mercury vapor may have acted in any one of three ways. The mercury may have acted chemically on the selenium so as to form a selenide, it may have acted catalytically in a way to alter the equilibrium of the selenium components, or it may have been merely entrapped in the selenium, without otherwise essentially altering its electrical properties.

One basis for the belief in the formation of a selenide at this stage of the experimenting lay in the statement, in Watt's Dictionary of Chemistry, that mercuric selenide is formed when mercury and selenium are heated together. However I noted that mercury did not freely combine with selenium, even when the latter was heated to its melting point.

If the mercury were trapped in the selenium by some absorption process so as to form a kind of solid solution, we would at once have an explanation of the high conductivity that always accompanies this light-negative property. Perhaps the light action merely alters the form of the crystals in all varieties of selenium similarly, and in this light-negative variety it thereby breaks the conducting film of mercury. This is a simple and apparently satisfactory explanation. It readily accounts for the irregularity and non-uniform behavior of the new selenium form. However it does not explain why light-negative selenium should be produced in the presence of mercury vapor, under conditions that would not produce any light sensibility at all in the absence of mercury vapor.

Should the mercury vapor act catalytically, so as to alter the rates of change of the existent components in the selenium, we have at once a satisfactory explanation. The first difficulty in the way of this explanation is the possible formation of a selenide. More will be said later concerning these theories.

THE EFFECT OF UNHEATED MERCURY VAPOR ON LIGHT-POSITIVE SELENIUM.

There was considerable uncertainty in the last experiment as to whether the mercury vapor at the high temperature may not have acted on selenium by chemical union. If such chemical action did not take place then it seemed reasonable to hope that mercury vapor at room temperatures might transform light-positive selenium into light-negative selenium. This is particularly consistent with the view that in the light-negative selenium the conducting material is essentially mercury, which is broken and altered by the selenium crystals changing form under the action of light.

Accordingly two small cells, made by dividing a regular size Giltay cell into parts, were placed in an apparatus connecting with a Gaede vacuum pump. The resistance of each sample was upwards of twenty million ohms, in the dark, and possessed the usual sensibility to light. After being kept in a vacuum of less than .01 mm. for twenty minutes there was no apparent change in resistance, but after being in the vacuum for twelve hours the resistance had fallen to 40 ohms. At first the irregularity of behavior when illuminated resembled that of the light-negative samples previously described. The resistance was so unsteady that it was difficult to say just what action was due to the light. The cell was then placed in a kerosene bath. After resting thus for several hours, it showed consistent light-negative properties. The following is a sample of the observations taken with the selenium alternately in the dark and illuminated with a 16 c.p. lamp at 20 cm. distance.

Resistance in Dark.	Resistance in Light.
70.5	70.6
70.5	70.61
70.5	70.58
70.5	70.56
71.3	71.5

And after resting three months in the dark, the behavior is illustrated by these readings. The illumination was approximately that above.

Resistance in Dark.	Resistance in Light.
86.3	86.43
86.33	86.43
86.33	86.50
86.0	86.12
86.0	86.11

The curve in Fig. 1 shows the manner in which the resistance changes with the time of exposure. The rate of change is not nearly so rapid as that of a light-negative sample for which the curve is given in Fig. 9 of a former paper on the "Nature of Light-action in Selenium."[1]

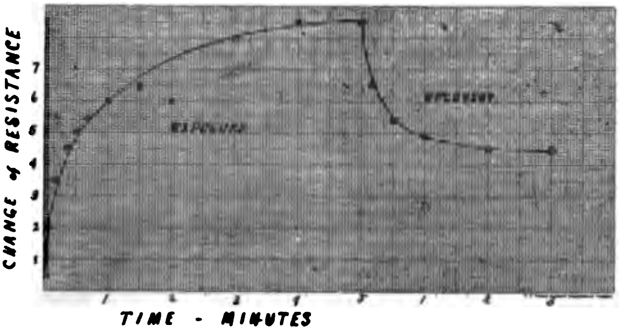

Fig. 1.

The difference in these two may be accounted for by the unequal light intensity in the two instances. At any rate the resistance begins to decrease at the instant of illumination in these new samples, and the change is so rapid at first that it is quite improbable that it is due to heat rather than light action. To definitely determine this point I hope soon to be able to map the sensibility of this variety of selenium throughout the spectrum, as Pfund[2] has done for light-positive selenium. Such a determination may also aid in a physical interpretation of the nature of the change of resistance.

The second sample referred to above was weighed before and after exposing it to the mercury vapor, to detect if possible the amount of mercury that was necessary to perform the observed transformation. Before placing in a vacuum and while the resistance was several million ohms the weight was 1.2527 gm. After exposing to mercury vapor in a partial vacuum for 16 hours, the resistance fell to 104 ohms. The weight had not changed by as much as 0.1 milligram. This result is not inconsistent with the supposition that the increase of conductivity arises solely from the direct conductance of the absorbed mercury vapor. For if it is assumed that the mercury vapor has the same conducting power as large masses of mercury, it can be readily calculated that a film of mercury 2.5×10^{-9} cm. thick would have been sufficient to account for the observed conductivity. Further the weight of such a film would be only 1.2×10^{-8} gm., which amount it would be impossible to detect by weighing. But even with this small amount of mercury inside the selenium the concentration of mercury would be about a billion times as dense as that in a saturated free space at the same temperature.

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[1] Phys. Rev., 33, p. 19.

[2] Phys. Rev., 34, p. 370, 1912.

THE ACTION ON POWDERED RED AMORPHOUS SELENIUM.

If in the Giltay cell, we could have been certain that all the selenium was acted upon, we would have known by the absence of increased weight that no chemical action took place. But as there was no obvious change of color or appearance, no estimate could be made of the extent of action of the mercury vapor.

The red amorphous selenium was exposed to the mercury vapor in a vacuum with the hope that a change in color would indicate the extent of the action. First a very small fraction of a gram of the red powder was scattered in the vacuum tube. Within half an hour after high vacuum was reached this selenium had turned black. The selenium was then packed between two wire electrodes. The resistance was fairly steady at 240 ohms. It was also light-negative, showing an increase of from 0.5 to 20 ohms. After heating for thirty minutes at 210° the resistance was reduced to 1.2 ohms. For a week following this heating the resistance was unsteady and slowly increased in value. However it did become steady after this interval and it was then quite light-sensitive. Several light-negative samples were made by packing this black selenium between wire electrodes. They were all of very low resistance and light-negative in character.

The fact that the red amorphous form did change its color to a distinct black, made it seem apparent that chemical action did not take place. If mercury selenide were formed, then when all the selenium changed to the black form it should increase in weight by the ratio of 79 to 200.

TWO SAMPLES OF RED SELENIUM WERE WEIGHED AS FOLLOWS:

Test No. 1.

Weight of glass tube container	1.066 gm.
Container + selenium	1.661
In vacuum 4 hours, 90 per cent. black	1.674
In vacuum 12 hours	1.667
In vacuum 10 hours longer	1.660

Test No. 2.

Weight of paper	0.514 gm.	
Paper + red amorphous selenium.	.808	
After 4 hours exposure to vapor	.803	
After 12 hours longer exposure	.803	
Exposure continued 6 hours	.808	selenium almost entirely black.
Exposure continued 4 hours	.797	mercury heated slightly.
Exposed to air 16 hours	.815	
Exposed 10 hours longer in vacuum	.801	
Exposed to air 3 hours	.813	

A third test was made using 2.013 grams of selenium. After exposure for about 60 hours the selenium was mostly blackened, and the weight had increased to only 2.033 grams. During exposure the effect of the mercury vapor did not penetrate far into the mass of powder. It was seldom blackened deeper than a millimeter, so that it was necessary to frequently stir a fresh surface for exposure. The second test showed what seemed to be the hygroscopic property of the selenium, by an increase in weight when it was exposed to the air. The fact that the selenium is blackened only near the surface, leads to the belief that the absorbed moisture does not play a very important part in the transformation.

The figures in these three tests apparently demonstrate that chemical combination between the selenium and the mercury vapor is quite inconceivable. If there were any definite measurable increase of weight due to the absorption of mercury vapor, it is masked by the variations in weight due to moisture and uncertain causes.

However I was deceived here by assuming that because the selenium was blackened in from 4 to 60 hours, and increased in weight by less than .03 gram that there could be no further action between the mercury and the selenium. The truth is that while it was blackened it was not all acted upon. After being exposed 1,230 hours in a high vacuum a sample weighing 0.565 gram increased in weight to 1.803 grams. When the vacuum was kept at the X-ray stage the increase was almost uniformly one milligram per hour for the first 1,000 hours, but during the next 200 hours, the weight increased more and more slowly. If mercuric selenide were formed the weight should have ultimately increased to 1.995 grams. The fact that this weight was not quite reached can easily be explained by the loss of selenium during weighings and by diffusion of its vapor in high vacuum, if not to the fact that sufficient time was not allowed for complete penetration and action.

I do not believe it right to assume at this time that the mercury vapor in a finely divided state in the selenium can have these light-negative properties, except for the action of light on selenium or the selenium compound.

One determination of the density of this new selenium gave 4.98, but this particular sample may have had some free mercury with it. With my arrangements it is a slow process to produce a sufficiently large quantity for an accurate determination of the density. A globule of mercury acts very rapidly on selenium surrounding it in a vacuum but at atmospheric pressure a mercury globule in contact with the red powder will not perceptibly color the selenium in several days. Later I hope to obtain the density more accurately. It will probably show the same density as mercuric selenide, which in fact it resembles.

It may be mentioned that powdered vitreous selenium when placed in an atmosphere of mercury vapor for 18 hours also assumes a high conductivity and the light-negative property. There is no apparent change in the color of this modification. It is rather strange that any powder should have such a high conductivity when rather loosely packed as the powders here were packed. The interaction between the mercury and the selenium arises probably more essentially from a property of the selenium. Powdered sulphur when exposed several days to mercury vapor at the same time the selenium was exposed showed no conductivity at all.

SUMMARY.

1. Mercury vapor acts on selenium in such a manner as to produce a very high conductivity and the light-negative property.

2. The mercury acts on the amorphous form and probably also on the other modifications so as to produce selenium of new characteristics. Permanent chemical compounds are probably formed between the mercury and the selenium.

3. A very easy and satisfactory method of making light-negative selenium cells is to place the amorphous selenium in a mercury vacuum until it becomes black, and then to press this black selenium between fixed electrodes.

4. The energy curve should be mapped out in order to gain evidence as to the similarity of action of light in this and light-positive selenium.

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THE

PHYSICAL REVIEW.

THE REFRACTION OF GASES AT DIFFERENT TEMPERATURES AND PRESSURES.

By H. D. Ayres.

Historical.

THE greater part of the early investigations on the subject of the refraction of gases was done with one of two aims in view: (1) the determination of the constants necessary for the correction of astronomical observations, and (2) the experimental verification of the constancy of the relation $(n - 1)/\rho$ = constant, which expression is derived from theoretical considerations in the emission theory.

In general, two methods have been employed in the investigations of the subject, namely: the prism method and the interference method. Much of the early work was done by the prism method. Dulong,[1] for instance, in 1826 used a hollow prism made from a metal tube, the ends of the tube being cut at an angle to its length and closed by means of plates of glass. He used a constant deviation, that is, ran the gas into the prism until the deviation in each case was the same. Arago in his earlier work used the prism. Gladstone and Dale[2] used the prism method in the work in which they established the constancy of the relation since known under their name.

Probably the first to apply the method of interference to the problem was Arago in 1821.

Since that time various modifications of the method have been used, probably the best known of which is that due to Jamin.[3] Mascart[4] working with the same apparatus made some refinements and rediscussed much of the earlier work of Jamin, showing that the observations could be more nearly expressed by the relation $(n - 1)/\rho =$ const. than by the equation $(n^2 - 1)/\rho =$ const. used by Jamin.

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[1] Annales de chim. et de phys., 2 ser., t. XXXI., p. 154, 1826.

[2] Phil. Trans., p. 887, 1858; Phil. Trans., 153, 1863, pp. 317–343.

[3] Ann. de chim. et de phys., t. LII., p. 1858; t. LXI., p. 385, 1861; Comp. Rend., 1856, p. 1191; Vol. 45, 1857, p. 1892.

[4] Ann. sc. de l'Ecole Normale sup., 2 ser., t. VI., p. 9, 1877; Comp. Rend., Vol. 78, pp. 617, 679, 801, 1874; Vol. 86, pp. 321, 1182, 1878.

Perreau[1] made some further modifications in the apparatus and studied the refraction and dispersion of hydrogen, carbon monoxide, and carbon dioxide, at room temperature, and pressures (differentially) to about five atmospheres.

Kayser and Runge[2] have used the prism more recently in connection with the grating.

Chappuis and Riviere[3] used a modification of Jamin's method, studying air, carbon dioxide, and cyanogen at ordinary temperature and at pressures up to 20 atmospheres. These gases were chosen because they differ widely in their densities and other physical properties. For air, the densities were computed by means of Van der Waal's equation and the constancy of the equation $(n - 1)/\rho =$ const. was found to hold within experimental errors.

For carbon dioxide, a formula from Clausius was used in computing the densities, the coefficients proposed by Sarrau being adopted. In the case of this gas a linear relation was found also.

Benoit,[4] in the course of an investigation on the comparisons of meter bars by means of the Fizeau dilatometer, had occasion to make correction for the refraction of the air. He tested the validity of the relation

$$n_1 - 1 = \frac{n_0 - 1}{760}(1 + 0.00367t)$$

by the use of his apparatus, making observations in vacuo and in air at a pressure of one atmosphere. His observations extended over a range of temperature from 0° to 80°. The results obtained verified the correctness of the expression for the pressure and temperatures used.

Apparently the only work so far published, in which the observations were extended to low temperatures is that of Scheel.[1] Observations were made at liquid air temperatures on atmospheric air, nitrogen, and hydrogen, at a pressure of one atmosphere, that is, readings were made in vacuo and at a pressure of one atmosphere. Assuming the correctness of the expression $(n - 1)/\rho =$ constant, Scheel deduces the values of the densities of the gases at liquid air temperatures from the refractive indices and compares the results with those obtained by other methods, and with the values computed from the gas laws. His conclusions were, that within the limits of accuracy of observation of his experiments, the constancy of the relation is established.

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[1] Ann. chim. et de phys., (7) 7, p. 289, 1896.

[2] Ann. der Phys., Vol. 20, p. 293, 1893; Abh. der Berl. Akad., 1893.

[3] Ann. de chim. et de phys., 6 ser., Vol. 14, p. 5, 1888. (For further modifications of Jamin's principles and applications of the apparatus see: Traver's Study of Gases, Ch. XXI.; Burton, W., Roy. Soc., Proc., 80, 1908, p. 390; Magri, L., Phys. Zeitschr., *6*, 1905, p. 629; Rayleigh, Nature, 81, 1909, p. 5191; various communications to Roy. Soc., Proc. and Phil. Trans., beginning in 1904, by Cuthbertson, C.)

[4] Jour. de Phys., 2 ser., 8, p. 451, 1889. (For other work on refractivity see: Nagaoka, H., "Relation between Index of Refraction and Density," Math. and Phys. Soc., Tokyo, 2, 19, pp. 293, 1905; Rentschler, H. C., "New Method of Measuring the Index of Refraction of a Gas for Different Light-waves," Astro. Phys. Jour., 28, p. 345, 1908; Siertsema, L. H. and de Haas, M., "Refractive Indices of Gases under High Pressures," Konink. Akad. Wetensch. Ams., Proc., *14*, p. 592, 1912.

Other expressions have been derived in the attempt to represent more closely the relation between the refractive indices and the density, the most notable of which is probably that arrived at independently by Lorentz[2] and Lorenz[3] and known as the Lorentz-Lorenz formula. By a simple approximation it passes into the Gladstone and Dale formula, and on the whole it seems to be an open question whether this more complex formula represents the facts more closely than the simpler expression of Gladstone and Dale.

It appears that the method of arriving at the proper value of the densities may be a matter of greater importance than the small differences in these formulæ. Including the usual method of taking the density as directly proportional to the pressure we have already noted three methods of deducing the densities. Whatever question may remain as to the superiority of this expression or that, it is evident that the relation between the refractive indices and pressure is not in all cases a linear one.

Method and Apparatus.

In the experiments to be described in this paper the interference method was used, and the change ensuing in the optical path of light traversing twice, the distance between two reflecting surfaces upon admitting a gas to the space between the surfaces was determined. If one represents by k the total shift of interference bands of wave-length λ, and by n the index of refraction of the gas, then one has the relation

$$n - 1 = k\lambda/2d,$$

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[1] "Bestimmung der Brechungsexponenten von Gasen bei Zimmertemperature und bei der Temperature der flussigen Luft," Verhand. der Deutsch. Phys. Gesell., IX. Jahrg., Nr. 1, 1907.

[2] Wied. Ann., *9*, 642, 1880; *11*, 77, 1880.

[3] Jour. de Phys., 447, 1885. (For other expressions connecting refractive indices and density see: Edwards, Amer. Chem. Jour., *16*, 625, 1894; *17*, 473, 1895; Nagaoka, Math. and Phys. Soc., Tokyo, 2, 19, 293, 1905. For further concerning Gladstone and Dale's formula see: Landolt, Lieb. Ann., Suppl., *4*, 1, 1865; Sutherland, Phil. Mag., *27*, 141, 1889.)

where d is the distance in cm. between the surfaces. At a given temperature, since d is constant and k depends upon the pressure, it may be noted that values of n are obtained for corresponding values of the pressure.

The general plan of the apparatus used and also many of the details of manipulation have been described in previous articles in this journal[1] on expansion work at low temperatures. Many modifications in the apparatus were required however, and after considerable preliminary work, testing different schemes in the attempt to obtain a vessel suitable for containing the interference apparatus and which would hold at liquid air temperatures a vacuum or a gas under considerable pressure, the form of the apparatus described below was finally used.

The interference apparatus consisted of two plates, 18 mm. in diameter; one, G_B (Fig. 1) was of black astronomical glass with one face plane and polished, the other, G_0, of optical glass, both faces being plane and polished and inclined at an angle of a few minutes to each other. A hollow cylinder of quartz Q about 15 mm. in length separated the plates, thus giving an optical path of some 30 mm. with a vacuum or a slightly longer path when the gas was admitted. The adjustment of these parts in the steel chamber as first used was as follows: a brass disk of diameter slightly less than the inside diameter of the chamber had one surface cut out, leaving a thin rim around the edge within which the black plate would rest. To the under side of the disk were attached three small spiral springs of such length that when the two plates and quartz cylinder were in place, the upper surface of the top plate projected slightly above the top of the chamber. Upon inserting the plate glass cover disk, the springs were compressed and the parts were thus held snugly against each other, the upper surface of the optical glass being in contact with the lower surface of the cover disk. With this arrangement, however, the fringe system was altered by tightening one or another of the screws by which the chamber was held in place, and upon cooling to liquid air temperature the fringes became very much distorted. It was thus evident that the optical system must be kept free from contact with the side of the chamber, at least toward the lower end. In order to accomplish this, the optical glass plate G_0 was attached to the cover disk G_P by Canada balsam being placed concentrically with it. A hollow brass cylinder C of diameter slightly greater than that of the disk and having a very thin wall was made, and the springs s, s for holding the quartz cylinder and black glass in place were mounted on the lower edge of this brass shell. Also to its lower end were soldered the three phosphor bronze springs S to rest on the bottom of the chamber and thus keep the top of the shell in contact with the plate cover disk. Since the optical glass G was fixed in place, it held the other parts in the center of the chamber by means of the brass shell. In this manner no contact was made with the outside chamber except through the springs, and the slight motion of the bottom of the chamber was not sufficient to cause a distortion of the fringe system through them.

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[1] Vol. 20, p. 38, 1905; Vol. 25, p. 58, 1907, and references in these articles.

But one serious trouble arose with this arrangement; at liquid air temperature the Canada balsam underwent some peculiar changes, becoming almost opaque at one temperature, or at one stage of the transitions. To remedy this, it was removed from the plates and three drops of solder placed on the outside of the brass shell very near the top to keep the optical system concentric. This arrangement proved satisfactory.

The chamber for containing the gas and interference apparatus was made from a piece of seamless steel tubing 2.2 cm. in diameter, and about 4 cm. long. Into one end of this was brazed a disk cut from a piece of strap steel, thus closing the end. Into the other end was ground a disk of plate glass G_p, the finishing being done with a very fine grade of carborundum powder. To the side of the tube was attached a piece of brass tubing for exhausting and admitting the gas. The chamber was mounted at the end of a quartz tube 18 mm. inside diameter and 23 mm. outside diameter and about 40 cm. long.

Fig. 1 is a drawing of the vertical cross section of the chamber. It shows also the plan used in attaching it to the quartz tube. A short piece of steel tubing, S_t, of diameter such that it fitted closely over the end of the quartz tube was screwed into and soldered to a steel disk S_D. The steel tube S_t was attached to the quartz tube by means of plaster of Paris.

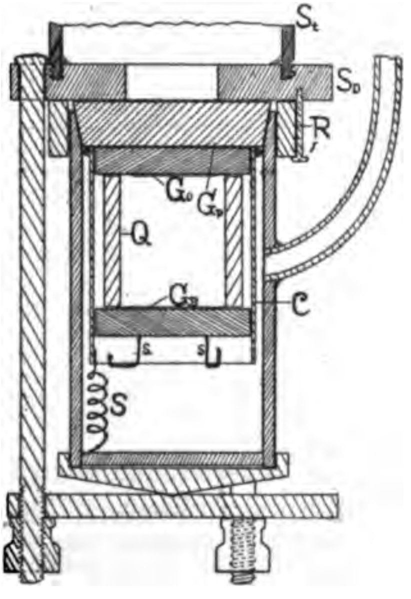

Fig. 1.

The steel disk S_D had an opening in its center 1 cm. in diameter for admitting the light to the chamber. The lower side of the disk was ground plane and the plate cover glass G_p rested against it with stopcock grease between the surfaces. In this manner the lower end of the tube was made airtight, though it was not exhausted. In order that the chamber take a position concentric with the opening in the steel disk, a brass ring *R* was attached to the former.

The upper end of the quartz tube was set by plaster of Paris in a brass tube *B*, Fig. 2, which was rigidly attached at right angles to a brass plate. This plate was screwed to the under side of the rectangular steel block *A*. This block had leveling screws and bolts for clamping it in position after all adjustments were made.

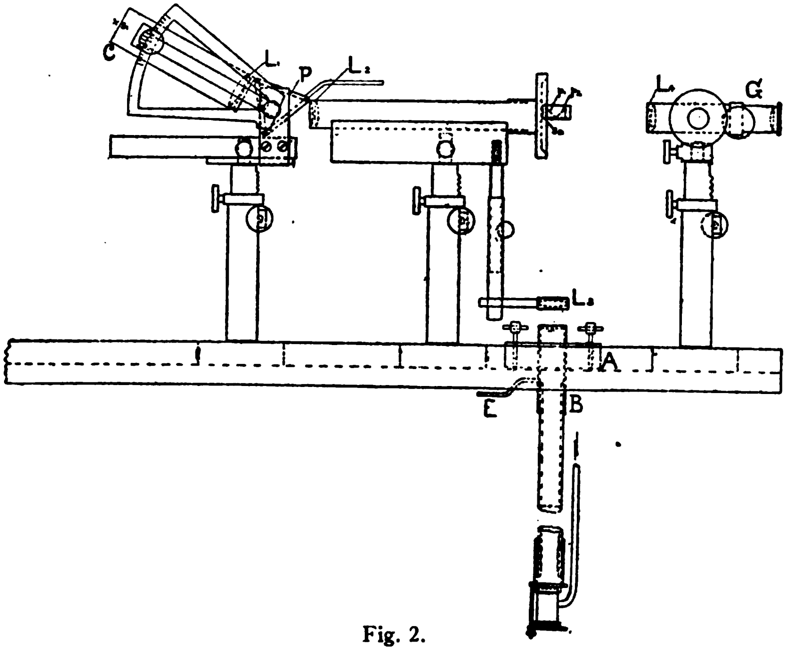

Fig. 2.

The air inclosed in the quartz tube was dry and at *E* was attached a tube with drying reagents so that, as the volume of the air in the quartz tube tended to decrease due to change in temperature, dry air was drawn in.

Fig. 2 is a side view showing the relation of the different parts of the apparatus. The whole was built on a heavy optical bench mounted at the side and about 20 cm. from the edge of a table. *C* was a collimating tube with a slit s_1 at the principal focus of the lens L_1. A flint glass prism was mounted at *P* in such a manner as to rotate upon an axis through its center. The lens L_2 brought the light to a focus at s_2, at which point was placed an adjustable spectroscope slit. The mounting of the prisms p_1 and p_2 not shown in the drawing, was such that a motion of translation in the vertical plane could be had, a rotation about an axis perpendicular to the spectroscope slit, a rotation about a second horizontal axis at right angles to this one, and finally, the whole mounting was hinged at the side and by one motion of the hand could be swung around out of the field in making other adjustments, and then brought back to exactly the same position. The light was reflected down by the prism p_1, rendered parallel by the lens L_3 which was mounted with a rack and pinion adjustment, was transmitted to the interference apparatus from which it was again reflected and again brought to a focus at the prisms and deflected horizontally by the prism p_2 to the observing telescope. This consisted of a short focus lens L_4 and a micrometer eye-piece fitted with cross hairs at right angles and double movable cross hairs. This telescope had a rack and pinion vertical adjustment and a lateral adjustment by means of a tangent screw.

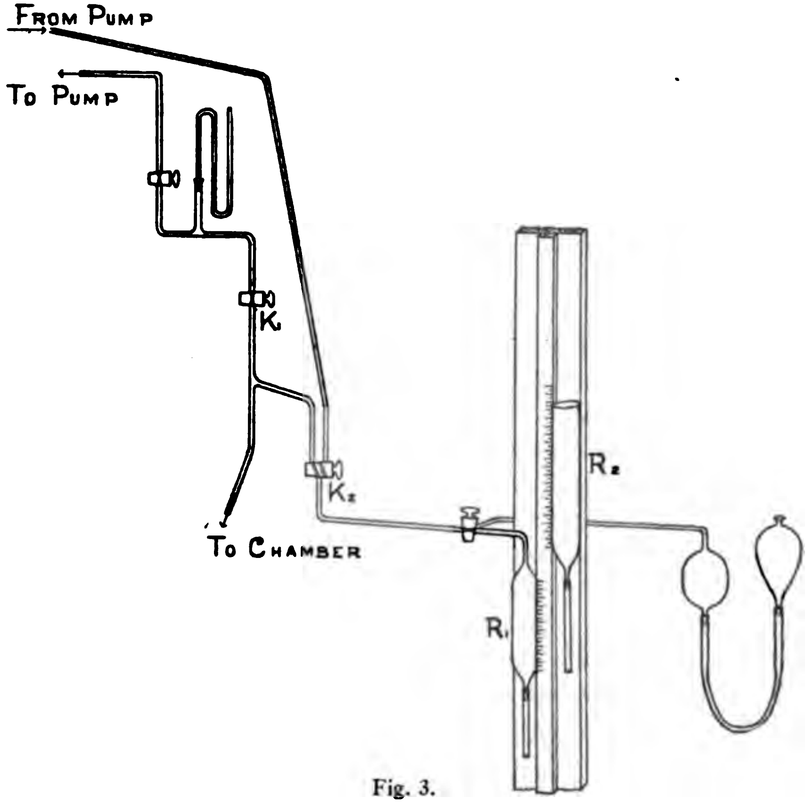

Fig. 3.

On the lower surface of the optical cover glass was cut a small circle about 1 mm. in diameter, and the fixed cross hairs in the eyepiece were set tangent to this circle. Such a circle is easily obtained by mounting the glass in the chuck of a small lathe and while rotating slowly, bring a diamond point against the surface of the glass, using a suitable rest.

The gas circuit is shown in Fig. 3. A mercury pump was placed at the side of the optical parts away from the table and connections made to it above the part of the apparatus just described. The parts shown in the diagram were mounted on the table near its end, being thus placed at the right of the optical parts, and the two principal stopcocks K_1 and K_2 were within easy reach while observing at G, Fig. 2. R_1 represents a cylindrical glass reservoir about 3 cm. in diameter and 30 cm. long; R_2 the mercury level reservoir was of the same diameter but somewhat longer. Both of these were mounted on the front side of a piece of studding extending to the ceiling. R_1 was mounted in a fixed position with its upper end a little above the top of the table.

R_2 was mounted on a carriage which could be moved up and down the timber by means of a cord passing over a system of pulleys at the ceiling. These cylinders were connected by pressure tubing which was wrapped with cord to prevent undue extension when cylinder R_2 was raised. Along the center of the timber were mounted meter bars for measuring the difference in height of the mercury columns. The readings upon these were made in a manner similar to that in reading an ordinary barometer. That is, brass collars of thin sheet brass were made of diameter a few millimeters greater than the diameter of the glass cylinders and these collars were mounted to move easily up and down over the cylinders. The lower ends of the collars were finished with pointers extending 1 or 2 mm. over the edges of the meter bars, also the lower edge of the collar and the lower edge of the pointer were in the same horizontal plane. The surfaces back of the cylinders were of such character as to give diffuse reflection. In reading, the collar was brought down until light could just be seen over the surface of the mercury, and the corresponding point on the meter bar read off. In this manner pressure readings could be made to an accuracy greater than 0.5 mm., but since the coefficient of expansion of the meter bars was not accurately known, nor to what extent, if at all, they were affected by the relative humidity, no attempt was made to read closer than 0.5 mm., and the final readings are given to the nearest mm.

In interference work where a large path difference is used, probably the most satisfactory light is the green light of the Cooper-Hewitt mercury lamp. This was used in the preliminary work, though it was the intention to use a series of spectral lines in the final observations on the gases studied. No source of light was found satisfactory for the work however, so the Cooper-Hewitt lamp was used throughout the investigation, observations being made with the green and yellow lines. The mean of the wave-lengths of the yellow lines was used in the computations.

Upon a change of pressure ensuing, it is obviously impossible to count the bands for more than one spectral line. To repeat the experiment under identical conditions and count the shift of bands for a second spectral line is also impossible. This difficulty may be overcome in two or three ways. In any case the fraction of the band nearest the fixed cross hairs is determined for each system of fringes at each pressure, *i. e.*, for the fringes of each spectral line used. Then, having counted during the change in pressure the whole number of bands moved of the wave-length chosen as the standard, the exact number including the fraction is known for this wave-length. Also the fraction of a band for the other, or for each of the other of the spectral lines used is known. If the total number of bands moved is small, the integral number corresponding to the fraction or to each of them, can usually be determined at once by inspection.

If the number of bands moved is large, and the number cannot be determined by inspection, a method similar to that given by Pulfrich[1] for the determination of the change of bands in dilatometer work by the use of two or three spectral lines instead of counting the bands may be used.

Let a = the whole number of bands moved of the wave-length chosen as the standard; let δ_0 = the initial fraction, and δ_0' = the fraction after the change in pressure has taken place. Let b, δ, and δ', represent the corresponding values for a second spectral line. Then $a + \delta_0' - \delta_0$ = the total number of bands shifted in the case of the first or standard wave-length and $b + \delta' - \delta$ = the total number of bands shifted for the second wave-length. Also

$$a + \delta_0' - \delta = N_0(1 - n_0)$$

and

$$b + \delta' - \delta = N(1 - n)$$

where N_0 and N are the total number of wave-lengths respectively in the path traversed by the light. Dividing the first equation by the second and rearranging, there is obtained

$$\frac{a + \delta_0' - \delta_0}{N_0(1 - n_0)} = \frac{b + \delta' - \delta}{N(1 - n)}$$

or

$$\frac{N}{N_0}(a + \delta_0' - \delta_0) = \frac{1 - n_0}{1 - n}(b + \delta' - \delta), \qquad (A)$$

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[1] Zeits. für Inst., 1893, p. 365.

$$\frac{N}{N_0}a = \frac{1 - n_0}{1 - n}(b + \delta' - \delta) - \frac{N}{N_0}(\delta_0' - \delta_0). \qquad (B)$$

Since $N_0 = 2d/\lambda_0$ and $N = 2d/\lambda$, one has $N/N_0 = (2d/\lambda)/(2d/\lambda_0) = \lambda_0/\lambda$ = a constant, j say. Also, for the present purpose, with a given gas the ratio $(1 - n_0)/(1 - n)$ may be considered as constant = k say. Then

$$ja = k(b + \delta' - \delta) - j(\delta_0' - \delta_0)$$

or

$$\frac{j}{k}a = b + \delta' - \delta - \frac{j}{k}(\delta_0' - \delta_0). \qquad (C)$$

A table can be formed the first column of which contains the successive values of a as 1, 2, 3, etc., the second column the integral parts of the product $(j/k) \cdot a$, as 0, 1, 2, 3, etc., and the third column the fractional part of the product. The quantity $\delta' - \delta - (j/k)(\delta_0' - \delta_0)$ must correspond to the fractional part. Therefore the whole number b can be obtained from the table at once.

It is obvious that this cannot be relied upon to the same degree of accuracy as the method referred to above, which is frequently used where the interference method is applied to linear measurements only. Notwithstanding this fact, equation (C) has been found very useful in the present investigation.

A more exact though more laborious method is to solve equation (B) directly for each separate case. The only unknowns in this equation are b and n and the latter can be substituted in terms of b and N, and b thus determined.

TEMPERATURE MEASUREMENTS.

For those observations made at 0°, the apparatus was packed in powdered ice in a Dewar cylinder. Under these conditions, of course no question exists as to the constancy of the temperature nor of its absolute value. For the observations made at liquid air temperatures, a platinum resistance thermometer was used to determine the temperature. The wire of this thermometer was mounted by threading it through small holes punched in thin strips of mica, then other strips were laid on these and rolled into a ring about 3 cm. in diameter. Two leads were fused to each end of the thermometer wire. The ring was tied to the outside of the chamber. Since the chamber and thermometer were completely immersed in the liquid air it seems very probable that the temperature of the enclosed gas was that indicated by the thermometer.

The thermometer was calibrated by observing its resistance in steam, in ice, and in liquid oxygen. Callendar's formula was used, the δ being computed by means of the values of these resistances.

One series of observations was made on carbon dioxide at − 78°.3 C. This temperature was obtained by immersing the chamber in a mixture of CO_2 snow and alcohol.

It may be noted that for the observations at liquid air temperature the values of the indices obtained upon decreasing the pressure are slightly greater than those obtained upon increasing the pressure. This is due to the slight rise in temperature resulting from the evaporation of the liquid air during the progress of the readings. Except in one or two cases especially noted, this change was slight. The temperatures given at the head of the tables are the mean temperatures where the variation amounts to as much as one and one half or two tenths of a degree.

During the preliminary work on the apparatus a number of readings were made on atmospheric air, mainly at pressures of about one atmosphere. The carbon dioxide and water vapor were removed from the air. Some of the observations were made at room temperature and some at 0° C. Reducing the former to 0° and all to 76 cm. pressure by means of the relation $(n_{t,\,p} - 1)/\rho_{t,\,p} = (n_{0,\,76} - 1)/\rho_{0,\,76}$, there is obtained by taking the mean of a number of these the value 1.000 2922 for the index of refraction of the green mercury line, and 1.000 2914 for the yellow line, with a probable error of 0.000 0003. In some of these readings the pressure was obtained from roughly balanced mercury columns and may have been incorrect to 1 or 2 mm. If a corresponding series had been made when the apparatus was in its final working condition, the probable error would certainly be very much less.

The value of the index of the D-line obtained by means of a dispersion formula from the above stated values is in very good agreement with the values tabulated by Scheel.

Two or three sets of observations were also made on air at liquid air temperatures, one of which is given in the table below. The Dewar cylinder used to contain the liquid air was a poor one and the liquid air evaporated rapidly, thus causing a considerable rise in temperature during the course of the readings. The first temperature was read near the beginning and the second temperature at the conclusion of the observations.

Atmospheric Air. −189°.0, . . . − 188°.0 C.

Pressure.	**Green.**		**Yellow.**	
	Bands.	$(n-1)\cdot 10^7$.	**Bands.**	$(n-1)\cdot 10^7$.
73.5	52.42	9,610	49.37	9,577
00.0	——	——	——	——
50.7	35.69	6,543	33.68	6,533
73.5	51.91	9,516	48.92	9,490
91.4	64.91	11,899	61.16	11,864
73.5	51.78	9,496	48.78	9,466

The values of the indices of air at liquid air temperature are also in good agreement with those obtained by Scheel, the only values available for comparison.

Preparation of the Gases and Observations.

Hydrogen.

Aside from the numerous preliminary observations on air, the first gas studied was hydrogen. It was obtained from a cylinder of electrolytically prepared gas, and an attempt was made to remove the traces of oxygen, carbon dioxide, and water vapor. A series of observations was made at liquid air temperature, the pressure being carried only to 192 cm. of mercury. This gas was then replaced by another quantity, which was more carefully prepared. After making a large number of observations on it, in order to know definitely regarding its purity, analyses were undertaken. These were made by means of the explosion pipette. The hydrogen proved to be very impure. Whether the contamination occurred at the time of the preparation of the gas, or from a leak in the pump during several days elapsing before the analyses were made, could not be determined, but probably resulted largely from the latter cause. Some trouble at one stopcock in the pump was remedied and another quantity of gas prepared, greater care being used in its preparation.

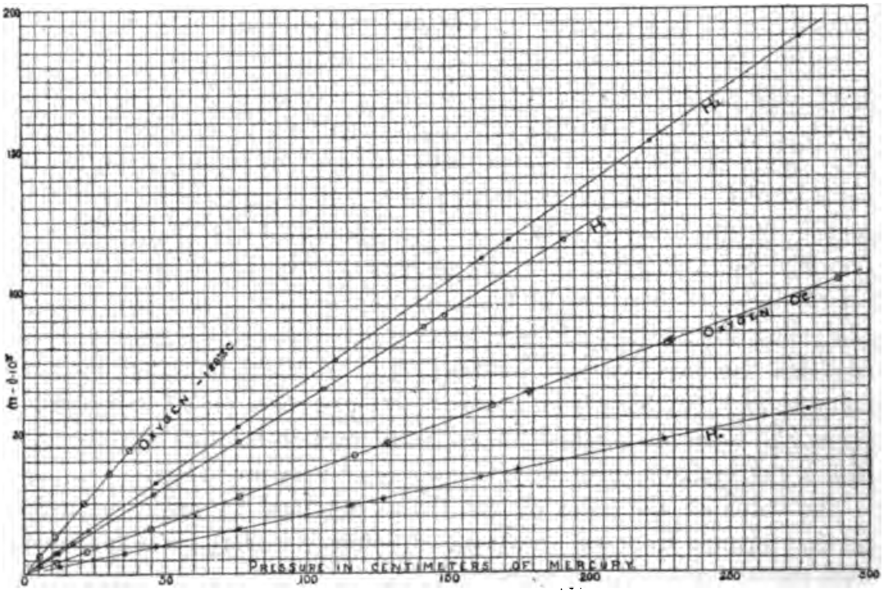

Fig. 4.

With this, one series of observations was made at — 191°.1 and one at 0°. These observations are given in the table, and the corresponding curves shown in Fig. 4. Analyses again made at the end of the work on one sample of gas drawn from the pump at the time of preparing the gas and on samples drawn at the conclusion of the observations gave the same results, and showed that this gas was also impure. The results were: hydrogen 88 per cent., oxygen 2 per cent., and though no test was made for it, the remainder in all probability was nitrogen. While it is granted that the observations on this gas are of no great value, yet since the composition of the gas is known, they may be of some interest.

Oxygen.

The oxygen also was obtained from a cylinder of the electrolytically prepared gas. Analyses of the gas drawn directly from the cylinder showed about two per cent. impurity. A test for hydrogen showed about one per cent. present. The remaining impurity was probably largely nitrogen, due to the absorbed air in the water from which the gas was made.

Because of the difficulties involved, no attempt was made to remove the trace of nitrogen, but the gas was passed over red-hot copper to remove the hydrogen, over solid caustic potash and through drying tubes including a tube immersed in liquid air. A pump was attached and the whole system of tubes containing reagents exhausted several times after allowing oxygen to enter, in an attempt to remove all traces of gases formerly contained in the tubes. The pump and gas system was also washed out with the gas previous to filling. Before the observations were begun, samples of the gas were drawn from the pump and an analysis made. Analyses were again made at the completion of the work. These were in good agreement and showed between one and two per cent. of impurity.

Two series of observations were made, one at 0° and one at — 189°.3. The observations are given in the table and the corresponding curves shown in Fig. 4. The readings at the latter temperature were continued until liquefaction began.

Nitrogen.

The nitrogen was prepared from atmospheric air by the removal of the oxygen and the carbon dioxide. Air was passed through a series of tubes containing pyrogallol, calcium chloride, lumps of phosphorus, and through phosphorus pentoxide and through a tube immersed in liquid air. Tests were made for oxygen, and it was found that a relatively large per cent. of oxygen still remained in the gas after it had passed slowly through this system. Another reservoir was then arranged so that the gas could be passed back and forth over the phosphorus and the two drying tubes. This was continued until analysis showed only a small fraction of one per cent. of oxygen. At the completion of the observations on the nitrogen, further analyses showed about the same percentage.

Three series of observations were made on nitrogen; one at 0°, and two at liquid air temperatures. At 0° the gas is well above its critical temperature, Boyle's Law is applicable, and the relation between $n - 1$ and the pressure is a linear one, or what amounts to the same thing, the relation between $n - 1$ and the density times a constant. In the case of the observations at liquid air temperatures, considerable deviation from linearity is found commencing at about one atmosphere. (See Fig. 5.) Curve (1) shows a little irregularity in the observations. The series was repeated with liquid air which had been allowed to stand for twenty-four hours, thus enabling one to work at a slightly higher temperature. These readings are shown in curve N (2). It may be noted that the observations were extended to a higher pressure before liquefaction occurred. The general form of curve is the same.

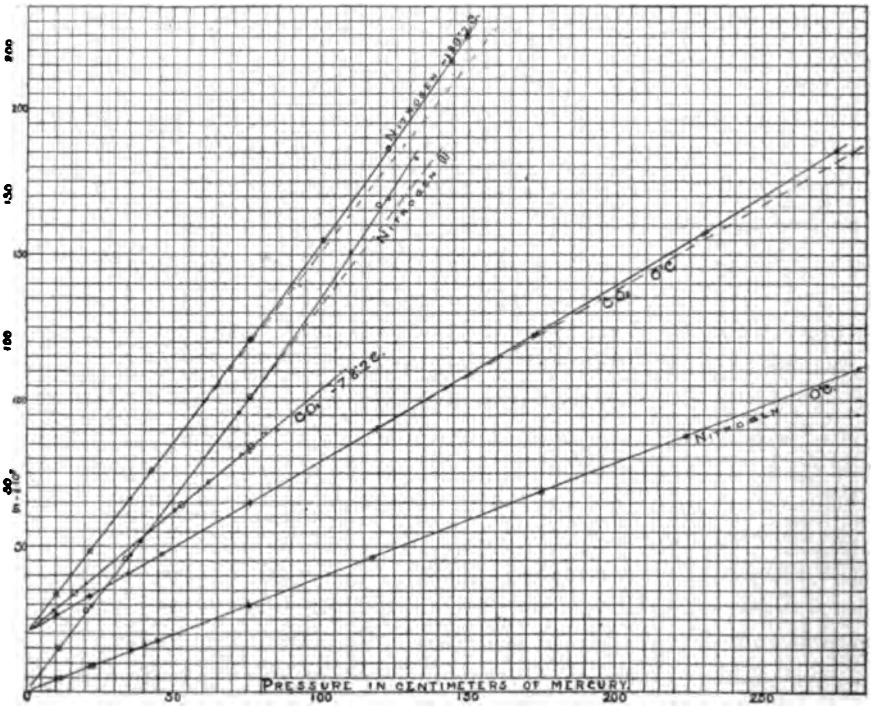

Fig. 5.

Carbon Dioxide.

Travers[1] would lead one to think that very pure gas can be obtained from the commercial product sold in steel cylinders. Acting upon this assumption, gas from a cylinder was passed through drying tubes and frozen in a tube with closed end immersed in liquid air. This tube was also connected with the pump and gas circuit, and upon closing the connection to the tube and opening that from the tube to the pump it could be exhausted to the vapor pressure of the carbon dioxide at liquid air temperature, thus removing air, etc., contained in the gas. Upon removing the tube from the liquid air and allowing its temperature to rise, the carbon dioxide would pass over into the pump and gas circuit. Analysis of the gas prepared in this manner showed about 75 per cent. carbon dioxide. An analysis of the gas direct from the cylinder showed about 95 per cent. carbon dioxide. The only explanation of this appears to be that the gas probably came from Saratoga Springs and contained one or more of the marsh gas series having a higher vapor pressure than the carbon dioxide. Consequently when the frozen mixture was removed from the liquid air, a mixture was obtained containing less carbon dioxide than the gas from the cylinder.

A Kipp generator was next set up and carbon dioxide was generated from acid on marble and purified in the same manner as that just described, except that there was added to the system of drying tubes a tube immersed in carbon dioxide snow and alcohol to remove further traces of moisture. The pump and gas system was washed with the gas as in the preceding cases. Analyses of samples of the gas thus prepared taken from the pump before the observations were begun, all showed about one half of one per cent. of impurity, In this respect the results were more satisfactory than in the case of any of the other gases.

Two series were made at 0° and one at − 78°.2. In the case of the former temperature, the circles on the curve represent the readings for one series and the crosses those for the other. It may thus be seen how closely the observations agree. Furthermore the second series was made on a different mass of gas.

For the higher pressures at 0° there is a very appreciable deviation from linearity.

In the case of the curve at − 78°.2 the readings were continued until condensation occurred, then the pressure was decreased somewhat and new readings taken, then the pressure again increased and so on. In this way a number of observations in that region was obtained. These are indicated in various ways in the diagram. The variation of the values is rather large, due in part to the error of observation, as some of the readings were obtained with difficulty, two thirds or more of the field being obscured by the carbon dioxide snow upon the surfaces of the glass plates. Also the pressures could not be read with great exactness under such conditions because of the changes in volume taking place.

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[1] Study of Gases, p. 49.

Hydrogen (1). *−187°.5 C.*

Pressure.	Green.	
	Bands.	$(n-1)\cdot 10^7$.
5.6	1.91	350
12.0	4.09	750
17.4	5.99	1,098
45.8	15.37	2,818
106.7	35.69	6,543
141.1	47.59	8,724
191.8	64.38	11,802
149.4	49.89	9,146
76.1	25.19	4,618

Hydrogen (2). *−191°.1 C.*

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.3	4.30	788	4.02	779
22.7	8.49	1,556	8.00	1,552
46.7	17.56	3,219	16.40	3,181
76.0	28.37	5,201	26.59	5,158
110.7	41.38	7,585	38.88	7,542
162.3	60.86	11,157	57.01	11,059
171.9	64.37	11,807	60.38	11,713
222.0	83.38	15,292	78.53	15,182
275.5	103.48	18,986	97.47	18,908
221.9	83.14	15,248	78.30	15,189
171.5	64.14	11,765	60.43	11,723
122.3	45.64	8,365	42.95	8,331
75.5	28.08	5,155	26.47	5,135
36.2	13.51	2,484	12.68	2,460
5.5	2.14	392	2.02	391
11.8	4.49	823	4.19	813
23.2	8.72	1,599	8.18	1,587
31.7	11.85	2,172	11.10	2,153
76.1	28.32	5,195	26.51	5,143

Hydrogen (2). 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
12.8	1.45	266	1.29	250
24.4	2.81	515	2.62	508
35.6	4.04	741	3.76	729
76.15	8.62	1,580	8.10	1,571
116.0	13.08	2,398	12.30	2,386
162.6	18.29	3,353	17.26	3,348
226.5	25.52	4,678	24.06	4,666
277.7	31.25	5,729	29.41	5,705
226.2	25.47	4,669	24.02	4,660
174.3	19.66	3,604	18.51	3,591
127.3	14.28	2,618	13.48	2,615
76.0	8 57	1,571	8.06	1,563
46.6	5.22	957	4.96	962
25.5	2.90	532	2.76	535
0.0	—	—	—	—
28.4	3.23	592	2.99	580
76.1	8.60	1,576	8.11	1,573

Oxygen 0° C.

Pressure.	Bands (Gr.).	$(n-1)\cdot 10^7$.	Bands (Yl.).	$(n-1)\cdot 10^7$.
11.6	2.32	426	2.19	427
22.2	4.31	790	4.09	793
44.9	8.72	1,599	8.17	1,585
76.2	14.83	2,718	13.98	2,712
117.3	22.84	4,187	21.42	4,155
165.9	32.29	5,919	30.38	5,893
227.6	44.29	8,119	41.68	8,085
288.7	56.35	10,329	52.00	10,289
229.1	44.76	8,205	42.16	8,178
178.7	34.67	6,356	32.71	6,345
128.9	25.14	4,609	23.69	4,595
76.3	14.92	2,735	14.05	2,725
44.8	8.79	1,611	8.29	1,608
13.9	4.76	873	4.45	863
0.0				
76.7	14.98	2,746	14.15	2,745

Temperature, − 189°.9 C.

5.4	3.62	664		
11.0	7.24	1,327		
21.2	13.69	2,510		
30.2	19.45	3,565		
37.2	23.89	4,380		

Nitrogen. 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10$.
11.7	2.55	468	2.36	458
22.6	4.87	893	4.58	888
44.8	9.58	1,756	9.00	1,746
75.7	16.20	2,970	15.27	2,962
117.5	25.13	4,607	23.63	4,584
175.4	37.49	6,873	35.32	6,851
224.0	47.95	8,790	45.16	8,760
282.8	60.46	11,083	56.95	11,047
223.9	47.90	8,781	45.14	8,754
174.8	37.40	6,858	35.24	6,836
118.4	25.34	4,645	23.82	4,621
75.6	16.21	2,970	15.23	2,954
36.0	7.74	1,419	7.29	1,414
0.0	—	—	—	—
10.4	2.29	420	2.15	417
21.4	4.64	851	3.98	838
40.7	8.75	1,604	7.88	1,594
75.6	16.17	2,964	14.89	2,954

Nitrogen. − 191°.6 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.0	8.17	1,498	7.59	1,472
20.2	15.19	2,785	14.22	2,758
33.9	24.91	4,566	23.36	4,532
75.8	56.42	10,343	52.09	10,105
119.6	91.07	16,695	84.70	16,430

− 190°.6 C.

72.6	53.21	9,754	50.20	9,738
35.6	25.67	4,706	24.18	4,691
0.0				
10.8	7.86	1,441	7.37	1,430
22.2	16.06	2,944	15.16	2,941
39.0	28.11	5,153	26.44	5,129
76.3	55.82	10,233	52.61	10,205
110.4	82.28	15,083	77.59	15,052
123.0	92.28	16,924	87.03	16,883
132.3	99.77	18,299		

Two hours elapsed between the first and second sets of the above readings.

In the curve, $N(1)$, Fig. 5, the point for the pressure of 75.8 cm. pressure in the first set should be four tenths of a division higher, and the point for the pressure of 72.6 cm. of pressure in the second set should be between three tenths and four tenths higher.

Nitrogen. − 189°.2 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$
10.1	7.27	1,333	6.81	1,321
21.9	15.72	2,882	14.82	2,875
42.8	30.49	5,589	28.71	5,569
76.4	55.09	10,099	51.87	10,062
101.0	73.60	13,493	69.35	13,453
122.8	90.69	16,625	85.45	16,576
143.5	107.08	19,629	100.87	19,567
149.5	111.81	20,497	105.45	20,458
143.4	106.98	19,611	100.83	19,560
122.8	90.50	16,590	85.32	16,551
100.9	73.48	13,470	69.29	13,441
76.2	54.77	10,040	51.64	10,018
35.5	25.19	4,618	23.74	4,605
0.0				
76.7	55.02	10,086	51.86	10,060

Carbon Dioxide. 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
10.4	3.44	631	3.26	632
21.7	7.04	1,291	6.66	1,262
46.3	14.91	2,733	14.02	2,720
76.3	24.54	4,498	23.12	4,485
119.5	38.59	7,074	36.39	7,061
171.9	55.90	10,248	52.67	10,217
230.3	75.28	13,800	70.89	13,752

Series No. 2.

10.9	3.50	642	3.33	646
21.6	6.97	1,278	6.54	1,269
34.9	11.19	2,084	10.46	2,029
76.3	24.45	4,482	23.00	4,462
119.1	38.39	7,038	36.15	7,013
173.1	56.23	10,308	52.91	10 264
229.6	74.91	13,732	70.48	13,672
274.9	90.05	16,508	84.81	16,452
228.8	74.64	13,683	70.32	13,641
173.1	56.20	10,302	52.91	10,261
118.6	38.31	7,023	36.03	6,989
75.8	24.34	4,462	22.86	4,435

Carbon Dioxide. — 78°.5 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
16.6	7.53	1,380	7.10	1,377
53.0	24.10	4,418	22.74	4,411
76.6	35.10	6,434	33.06	6,413
0.0	——	——	——	——
9.3	4.23	775	3.98	772
20.6	9.33	1,710	8.78	1,703
51.0	23.04	4,224	21.72	4,213
76.1	34.53	6,330	32.49	6,303
85.4	38.13	6,990	35.97	6,978
73.4	33.33	6,110	31.40	6,091
81.1	37.25	6,829	35.07	6,803
73.0	33.27	6,099	31.39	6,089
62.4	28.48	5,221	26.80	5,199
50.7	23.09	4,233	21.75	4,219
0.0	——	——	——	——
76.1	34.01	6,235	32.02	6,211

From the various curves we have seen that within the limits of accuracy of observations of the experiments, the relation between the indices of refraction and the pressure is a linear one, except for the case of carbon dioxide at 0° and for nitrogen at liquid air temperature. In other words, the relation between the refractive indices and the density as computed by Boyle's law is a linear one.

For the carbon dioxide at 0° and the nitrogen at liquid air temperature the densities have been computed by means of van der Waal's equation. The values of the constants a and b of the equation were obtained from the critical pressure and temperature of the respective gases. For carbon dioxide the values of the critical pressure given in the tables vary rather widely. A value of 5,700 cm. of mercury was chosen, and 304° abs. as the temperature. By the use of these values were obtained, $a = 137{,}000$ and $b = 0.942$. The curve showing the relation between the resulting densities and refractive indices is given in Fig. 6. The points fall very accurately on a straight line.

The critical values of nitrogen as used were, 2,660 cm. and 146° abs. The resulting values of the constants are $a = 126{,}070$ and $b = 1.325$. The densities were computed for the pressures in the series $N(2)$. In this series the values of the pressures for increasing values and those for decreasing values are very near each other, in some cases identical. Where they are not identical the mean of the two was taken, also the corresponding mean of the indices of refraction in plotting the curve.

The curve is shown in Fig. 6. The points lie on a straight line except the last two.

In order to compare further the variation of the refractive indices with the densities as obtained by the two methods, and also to compare the formula of Gladstone and Dale with the Lorentz-Lorenz formula, the table on page 182 is given. The first column contains the pressure and the fourth the corresponding refractive indices; the second column contains the densities as obtained by Boyle's law, the third the densities as obtained by using van der Waal's equation, the fifth the values of the constant as given by Gladstone and Dale's expression, using the values of the densities in the second column, the sixth the values of the constant as given in the third column, and the seventh and eighth columns the corresponding values of the constant of the Lorentz-Lorenz formula.

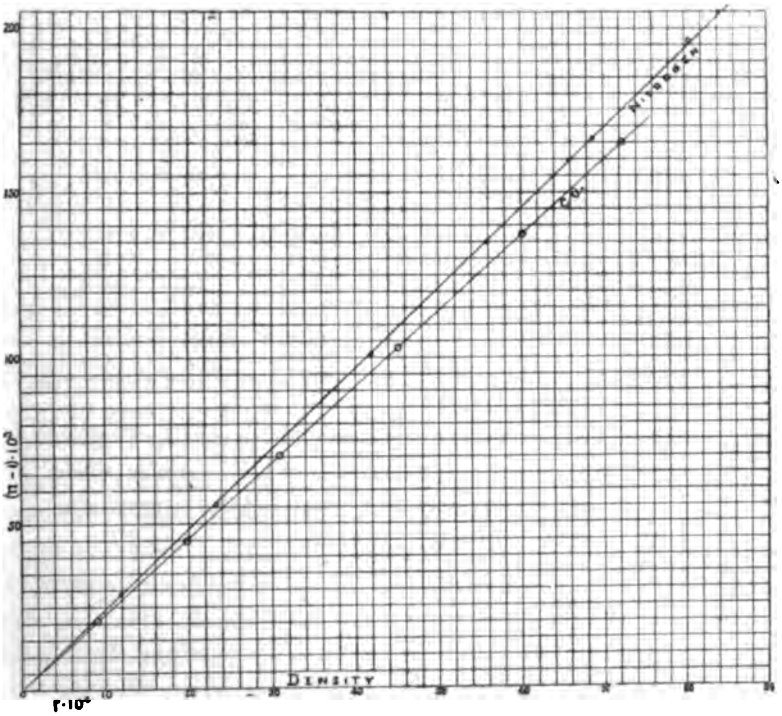

Fig. 6.

It may be noted that the variation of the values in the last column is two per cent. and the variation of those in the sixth column also two per cent.

It may be of interest to state that for nitrogen at 0° C. (excluding the two lowest pressures), computing the densities by Boyle's law and using the Gladstone and Dale expression, the values of the constant vary only about two tenths of one per cent.

Nitrogen. *−189.2° C.*

Pressure in Cm. Mercury.	Densities Obtained by Using Boyle's Law.	Densities Obtained by Using van der Waal's Equation.	Indices of Refraction.	Values of the Constant in Gladstone and Dale's Expression Using Densities from Column Two.	Values of Constant in Gladstone and Dale's Expression Using Densities from Column Three.	Values of the Constant in the Lorents-Lorenz Expression Using Values of the Densities from Column Two.	Values of the Constant in the Lorents-Lorenz Expression Using Values of the Densities from Column Three.
10.1	0.000543	0.000544	1.0001333	0.2455	0.2450	0.1637	0.1633
21.9	.001177	.001187	.0002882	.2448	.2434	.1632	.1623
42.8	.002301	.002328	.0005589	.2429	.2401	.1619	.1600
76.4	.004101	.004194	.0010099	.2462	.2408	.1641	.1605
101.0	.005424	.005589	.0013493	.2481	.2414	.1658	.1609
122.8	.006601	.006874	.0016625	.2518	.2419	.1678	.1612
143.5	.007709	.008054	.0019629	.2546	.2438	.1697	.1624
149.5	.008036	.008411	.0020497	.2551	.2437	.1699	.1623

In conclusion the writer wishes to express his thanks to Professor E. L. Nichols for many kindnesses and to Professor J. S. Shearer, under whose direction the work was undertaken, for many helpful suggestions.

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THE THERMAL COEFFICIENT OF CONTACT ELECTROMOTIVE FORCE.

By Harry C. Burbridge.

In looking back over the development of electrical knowledge we find many experimenters who have made a study of contact electromotive force. Their work has been extensive in its range and carefully done and the discussion of it has contained the defense of many widely differing theories. Yet, with all the investigation that has been given to this subject, the effect of temperature upon the potential difference of contact has received but scant attention. A few investigators have attempted to determine it but their efforts, with one exception, have proven almost fruitless. It would seem unquestionable that this temperature effect would have an important bearing upon the explanation of the original phenomenon and that its determination is worthy of extended effort.

Peculiarly enough, from the first attempt ever made to measure this temperature effect came some of the most satisfactory results. This attempt was made by Cavallo,[1] an experimenter in England, at some time previous to the year 1795. He used the very simple means of dropping a piece of metal from his hand upon an insulated tin plate, shaking it off, and then by applying the plate to a multiplier, increased the charge sufficiently to be tested with an electroscope. This process would, of course, give the contact potential difference between tin and the metal used. He found in this way, zinc positive to tin and silver; bismuth negative to tin, but lead and platinum positive to it. On heating the different metals, he found zinc, tin, silver and bismuth to become more positive, while lead and platinum became more negative. It appears then that he placed most of the metals in their proper order both as to their potential and the change of it by increased temperature, though the magnitude of this change could not be measured with his apparatus. This, of necessity, terminated his work and it was not until 1879 that further attempts were made to perform this experiment. At that time Knott[2] made measurements on the potential difference between two plates of the same metal, one being heated. He found iron, copper, zinc, and tin to become negative when heated, and the effect to increase with the temperature. This change, however, was permanent, as it persisted after the metals were cooled, hence what he determined was the relation of a hot and oxidized surface to a normal one of the same metal. This then was not a true temperature effect and as his work ceased here it is of no practical value. Again in 1882, Von Zahn tried the same experiment, hoping to find it related to the Seebeck effect. His conclusions are not available.

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[1] Nicholson's Journal, Vol. I., page 184, 1802.

[2] Knott, Proc. Royal Soc. of Edin., No. 105, p. 362, 1879.

It is evident therefore that the data given by Cavallo nearly a century before are as valuable as these later data so that it is in the results of Erskine-Murray's[1] work alone that anything dependable is to be had regarding the temperature effect. The range of his experiments was not large either in the number of metals used or in the temperature differences. No temperatures were carried beyond 70° and some to only 30°. Also the determination of the temperature was very rough, being estimated by touching with the fingers in all plates except one.

When these conditions are considered in regard to the data given by Erskine-Murray, and it is remembered that these are the only data of any consequence that have been published, it would seem that the present endeavor to measure the temperature effect would be far from mere repetition. It was undertaken with the purpose of adding to the other data upon contact electrification, some reliable values of its temperature coefficient.

The method of the following experiments was essentially the same as that used by Erskine-Murray, namely, a null method. It differs from it, however, in one respect and in that same respect from all other experiments on the potential difference of contact. Instead of using parallel plates two telescoping cylinders were used, the inner being much shorter than the outer so that it could be put well inside it. No matter what theory of contact potential difference one holds to, it is agreed that between the two surfaces there is an electrical field. This form for the two metals was chosen therefore that the metal composing the inner cylinder might be wholly in the field of the other, and not partially so as in the case of plates.

A sensitive electroscope was tried at first but discarded in favor of a Dolazalek electrometer. The sensitiveness of this instrument more than compensated for its larger capacity, and its reliability left no question as to the advantage of its use. The heating of the inner cylinder was first done by raising it into a steam jacket but it proved more satisfactory to fill the cylinder with water and use an electric heater, and this method was followed throughout.

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[1] Erskine-Murray, Phil. Mag., Vol. 45, p. 398, 1898, "On The Volta Electricity of Metals."

The apparatus was arranged as shown in Fig. 1. The outer cylinder (*A*) was made of commercial sheet copper about 1.2 millimeters thick and formed into two half cylinders 94 mm. in diameter and 240 mm. in length. The halves were held together by two adjustable copper bands. The base (*B*) was turned from plate copper 8 millimeters thick and the outer part thinned to 5 mm., leaving a circular table 3 mm. high in the center, over which the cylinder (*A*) fitted. This base (*B*) rested on a triangular wooden table with three screw-feet for leveling. In the center of the base was a three-millimeter hole fitted with a hard-rubber insulator. Through this passed a No. 22 brass wire, the portion below the base being coiled into a spring to make the contact adaptable.

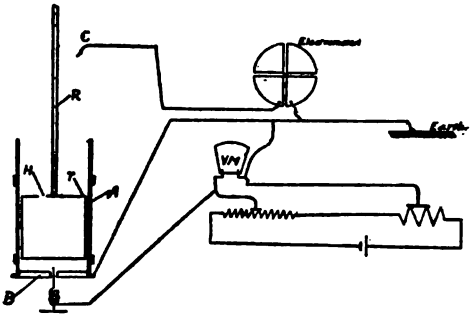

Fig. 1.

This construction of cylinder and base allowed for easy cleaning. On removing the cylinder (*A*), the base was unobstructed and the cylinder itself being in two parts, both inside and outside surfaces were readily accessible.

The different metals investigated were made into the form of hollow cylinders as (*I*), closed at both ends. They were each 86 mm. in length and diameter, thus leaving about 8 mm. between the walls of (*A*) and (*I*). These inner cylinders were cast from the metals used, with one end left open and a plate cast for this. Both parts were turned down to about 5 mm. thickness, the top plate carefully fitted in and then spun firmly in place. When necessary the inside edge of the top plate was coated with solder to insure a strong joint, but in such cases care was taken that no solder was exposed on the outer surface of the finished cylinder. In some cases where casting was not convenient or where a very pure, metallic surface was desired, cast cylinders were electroplated with the metal to be tested.

When in use, the cylinder (*I*) was carried on the vertical rod (*R*) which slid in guides. A cord fastened to the side of (*R*) raised and lowered this cylinder by passing over a pulley above the top guide and thence to a counter-weight hung over a second pulley at the edge of a table. On this table were placed the telescope and scale for use with the electrometer and also the voltmeter and potential divider. With this arrangement the cylinder (*I*) could be raised and lowered and the movement of the electrometer needle observed at the same time. Adjustable stop-blocks with rubber pads were placed on the rod (*R*) and were set to allow the cylinder (*I*) to be lowered as close to the base (*B*) as desired and raised to just touch the flexible wire contact (*C*) leading to the electrometer.

Each inner cylinder (*I*) had a rod of the same metal 13 mm. long screwed into the center of the top. Into this was screwed a wooden piece of about the same length and the wood in turn joined to the rod (*R*) by a connection of hard rubber. The rubber served to insulate the cylinder electrically, while the wood was found necessary to keep the rubber from being softened too much by the heat from the cylinder.

In the top of the inner cylinder (*I*) and near the center a hole (*H*) was bored large enough to admit a heater made from a quarter-inch fiber rod wrapped with No. 22 resistance wire. On the opposite side of the center and flush with the inner surface a smaller hole (*T*) was bored through which a stirrer or thermometer could be inserted. The stirrer was made of stiff wire with a strip of sheet metal soldered on one end at right angles and short enough not to strike the heater. By rolling the handle of the stirrer between the thumb and finger, the blade could be moved rapidly through the water in the cylinder at any depth. This rapid stirring allowed the cylinder to be heated very uniformly. When the desired temperature was reached the stirrer was replaced by a thermometer. The opening (*T*) was located with the purpose of bringing the thermometer as close to the outside surface as possible so that the temperature it registered would be closely that of the surface.

The potential divider was of 90 ohms resistance with a ten-ohm auxiliary of coarser wire to allow more delicate adjustment. One storage cell and these rheostats were connected in series and the potential difference between the sliding contacts on the rheostats was indicated by a voltmeter reading direct to .02 volt. Thus by estimating the tenths of a division the potential difference could be determined to .002 of a volt.

The needle of the electrometer was charged to 250 volts and with the scale distance used gave a deflection of 50 cm. to the volt. The ratio of its capacity to the capacity change on separating the cylinders (*A*) and (*I*) was such that the throw equalled what the permanent deflection would have been for the same difference of potential. Thus .01 of a volt between the quadrants gave a deflection of 5 mm. and this same difference between the inner and outer cylinders (*A*) and (*I*) gave a throw of 5 mm. From this it is evident that a throw of 1 mm. corresponds to .002 of a volt between the cylinders, which was the smallest quantity that could be read on the voltmeter. Though contact difference of potential is usually given to .001 of a volt there was nothing found to justify this. When it is considered that a clean surface at room temperature will often vary .003 or .004 of a volt in a few minutes, and when heated, as much as .006 or .008 inside of a minute, it will be seen how useless any effort toward accuracy to thousandths would have been.

The outer cylinder was carefully prepared by thoroughly cleaning with emery cloth, both the inner and outer surface of the walls and base, until every portion was bright. The surfaces were finished with the finest emery cloth and kept clean by handling only with soft, dry cloths. This left a surface almost polished in appearance, but covered with light scratches from the very fine particles of emery. It was expected that these surfaces would have to be repolished frequently, but this was not found necessary. By allowing nothing moist to come in contact with them no change could be noticed after the elapse of two or three months. The close agreement of the readings taken on the potential difference between the cylinder and a given metal, even when these readings were some weeks apart, indicated also that there was no change electrically. For surfacing the inner cylinders the finest emery cloth was likewise used. Their appearance was as described above for the outer cylinder. This surface was taken as standard, and all measurements were upon metal surfaces so prepared.

With this outer cylinder as the metal of reference, the procedure for taking a set of readings was as follows: a cylinder of the metal to be tested was put in a lathe and turned with the emery cloth held against it. The cloth was moved very little lengthwise so that the scratches were all nearly parallel to the base. On the ends the cloth was kept stationary so that all the scratches were concentric circles. The particles of metal clinging to the cloth were removed every few seconds by snapping with the finger and a fresh piece taken frequently to insure as clean a surface as possible. This process was continued until every part was bright, then a soft cloth was rubbed over the cylinder to remove all metallic dust and particles of emery. The cylinder was then reversed to complete the polishing, the finished end being wrapped in cloth to protect it from the jaws of the lathe.

The cylinder was then screwed firmly onto the sliding rod (*R*) and usually its potential with reference to the outer cylinder was determined at that time. It was then lowered into the outer cylinder and allowed to stand over night. As has been frequently noted before, the value immediately after polishing was not permanent, consequently sufficient time was allowed before taking a set of measurements to permit the potential difference to become more nearly fixed. On beginning a set of measurements the following day, readings were taken ten or fifteen minutes apart for a half hour or longer until the potential difference seemed quite constant. This was done because it was found that the first reading always indicated the inner cylinder more positive to the outer than was permanent. The potential difference would usually fall very rapidly at first, then more slowly to a quite permanent value in about twenty minutes. The reason for this is not apparent.

When this value was reached the temperature of the inner cylinder was taken by inserting a thermometer. The temperature of the outer cylinder was obtained by using a thermometer with its bulb resting against the base (*B*). Most of the bulb was exposed to the air but the cylinder was also, so that this seemed as good a means as was necessary to determine the average temperature throughout the cylinder. It proved sufficiently accurate to show that the radiation from the hot cylinder, though it was inside the outer one only long enough to make contact and be lifted out, continually warmed it. This increase in temperature amounted to as much as five or six degrees when the readings on the inner cylinder were taken as high as 90°.

With these records made, the heater was placed in the inner cylinder and the thermometer replaced by the stirrer. The current was allowed to flow through the heater for the time found necessary by trial to raise the temperature of the cylinder and its contained water about ten degrees. The stirrer was used continually that the whole surface of the cylinder might be heated uniformly. The heater was then removed, and the water well stirred and the stirrer removed. The potential divider was at once adjusted until on lifting out the inner cylinder and touching it to the contact point (*C*), the electrometer was unaffected. The potential difference was read from the voltmeter and a thermometer placed in the cylinder. The voltmeter reading and that of the thermometer against the outside cylinder were recorded, and that of the inner cylinder as soon as it reached its highest point. This gave the temperature of the inner cylinder immediately after the potential difference was measured so that the cooling during the time required to adjust the potential divider did not necessitate a correction. The cooling itself was never rapid enough to prevent the easy adjustment of the potential divider as, at the highest temperature, the rate was only one degree in four minutes which was usually longer than necessary to set the divider. This process was repeated until the maximum temperature was reached. The cylinder was then brought back to room temperature in intervals of approximately 10° by taking out some of the hot water and replacing it with cold. All readings were taken after each interval in the same manner as during the heating.

All the original data were corrected as found necessary when the instruments used were tested. The fixed points of both thermometers were determined and corrections made accordingly. In addition the readings of the one used in the inner cylinder were corrected for the length of the mercury thread exposed. This was done by putting the same length of the stem as went into the cylinder, into a steam bath and noting the difference between the reading then, and that when the whole length was immersed. The readings of the cylinder temperatures were then corrected by the fractions of this difference corresponding to the length of the exposed mercury thread. With these corrections probably no temperatures are in error by more than one or two tenths of a degree. Because of the corrections to the voltmeter readings they neither end in all odd nor all even numbers, but as stated before they are accurate to only 2 units in the last place.

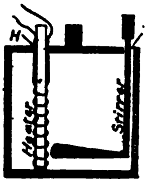

Fig. 2.

As would be expected, the temperature of the outer cylinder did not remain constant while a set of readings were being taken. This meant that the cylinder's potential changed somewhat from one measurement to the next and consequently, the potential difference observed was in error by the amount of this change. The correction to be applied would have been easily found had the coefficient of copper been known, but not being so, a proper method of determining it seemed difficult to find. It is not to be overlooked that placing the inner cylinder, at perhaps 80 or 90 degrees temperature, within a few millimeters of the outer copper base even for only a second or two necessary for each contact might easily heat the very surface of this base far above the temperature of the remainder. If then it is the surface that determines the potential difference, this effect might cause the readings to be considerably below the true value because the real temperature difference would be far less than the one measured. However, as there seemed no way to prevent this if it should exist and no way to measure it so that a correction could be applied, it is disregarded in the following.

After some consideration the following method of correcting for the temperature change of the outer cylinder appeared the most reasonable one to be applied. It was assumed that its temperature coefficient was the same as that of the inner cylinder made of copper. Then the four most consistent sets of data on the temperatures and the potential differences of the two copper cylinders were tabulated for increasing temperature only. Each number was subtracted from the one below it in its own column, thus giving a table of the change in voltage from each temperature reading on the inner cylinder to the following one, and also whatever increase in temperature the outer cylinder had taken on. Each of these potential changes were then corrected by proportion. Thus, if from the previous reading the potential had risen .008 volt, the temperature had increased 10.8°, and the outer cylinder at the same time had become 0.6° warmer, then the increase in voltage was not due to 10.8° because the voltage is measured from a base that has risen 0.6°. The measured rise in potential was then due to 10.8 less 0.6 degree, or 10.2°. Hence, if the base had not risen in temperature the voltage change would have been $(.008 \times 10^\circ.8)/10^\circ.2$ volts. This method of correction was applied to each change of potential and then by adding these differences the readings were obtained that would have resulted, had the outer cylinder remained constant in temperature. These values were plotted and the straight line drawn that best fitted each set of readings up to about 50° temperature. The slope of the line for each set was determined and the average of these slopes taken. This average value was then considered the temperature coefficient of the outer copper cylinder. All the readings of the potential difference were corrected by the use of this coefficient for the number of degrees which the outer cylinder differed from 20°. Thus all potentials given are with reference to this copper cylinder at 20° temperature.

In getting at the correction for the change in temperature of the outer cylinder it was assumed that the relation between the voltage and temperature was a straight line for the range used, of about 30°, and the data justified this assumption. However it would not seem allowable to assume a straight line relation for the whole range. When it is considered that a satisfactory explanation of the Volta effect has not yet been set forth, it would not seem worth while to hazard a guess as to the action that underlies the effect of temperature. Hence no form of curve can be assumed, and the variations from it considered merely errors of measurement.

Besides this, another difficulty arises in the interpretation of the results obtained, because the values are not uniform and consistent but widely varying. Despite the utmost care in preparation to have the surface always the same yet the potential difference at room temperature for the same metal against the copper outer cylinder would be quite different from one day's surfacing to another. This was not so serious a difficulty, as it was the change and not the absolute potential difference which was sought. The serious thing was the widely differing values of the temperature coefficient obtained which made a reliable determination of it most difficult. The temperature-voltage curve for a given metal, with falling temperature, neither came back accurately on the rising temperature curve, nor differed from it in any consistent way. Taken altogether, therefore, the data indicate that there is another agent or agents constantly in operation whose effects are a large fraction of those obtained from temperature. These effects are overlaid upon that due to temperature and the sum of these is all that the measurements can show. The continual action of these agents is illustrated by the following data:

Time.	Potential Difference.	
10:30	+.945	
10:40	+.923	Inner cylinder of zinc.
10:52	+.928	Both cylinders at room temperature.
11:21	+.948	
11:38	+.946	

The first rapid lowering is the effect previously mentioned, that obtained when the inner cylinder is first brought out after standing in the outer for some time. This effect was found in all metals used and was sometimes as large as .065 volt in magnitude. That it was the result of standing inside the outer cylinder is evident because at any time while the potential was diminishing, the decrease could be checked or even reversed by letting the inner cylinder remain in the outer one for ten or fifteen minutes. After standing outside for some time the potential would reach a minimum and then go through some such variations as are given above, without any apparent regularity and from no evident cause. The cylinder merely stood in the air of a closed room illuminated by daylight and was not even approached.

It would seem then that the only way to get at the effect due to temperature alone would be to consider these extraneous effects as following the law of probability. The most nearly true value of the temperature effect would accordingly be reached by averaging. All observations on the variation of potential difference at constant temperature would tend to justify this method of interpretation, and it will accordingly be used. The curves appended give the results from most of the data obtained but certain effects peculiar to each metal will be mentioned here.

Copper.—Erskine-Murray found that copper if heated above 80° seemed to begin oxidizing or at least this was the action supposed to take place. It must be understood that it does not alter the appearance of the surface in any noticeable way but the change is evidenced only by the fact that on cooling to room temperature the potential falls far below its value at the beginning. To assume that a slight oxidation has taken place seems the most reasonable explanation as oxidation of the surface will produce, a similar but larger effect. To locate the temperature at which this takes place in copper is somewhat difficult as in passing that point either when heating or cooling no marked change is to be noticed. It is determined only by the fact that if copper is heated above 80° its potential when cooled to room temperature again will be far below the value at the beginning, while if not heated to quite that temperature it will return practically to the original condition. The following data illustrate this action.

Potential Diff.	Temperature.	Potential Diff.	Temperature.
+.078	17.1	+.134	91.3
+.078	27.2	+.084	79.2
+.082	38.0	+.086	67.9
+.084	48.2	+.068	55.2
+.095	58.7	+.051	42.9
+.109	68.7	+.045	33.8
+.127	77.8	+.049	23:1
+.127	84.7		

Numerous trials located this oxidation point at closely 80°, the same as found by Erskine-Murray. The maximum temperature used in determining the true temperature effect is then always below 80°.

Zinc.—Zinc shows the same oxidation effect at 65° as copper does at 80° but it is much easier to locate the temperature at which the action begins. This is because at that point the potential begins to fall and increased temperature only increases the rate of fall. That this is not a change in the sign of the temperature coefficient is shown by the fact that in cooling the potential decreases continually and does not return through the values obtained in heating. In copper, it is evident that the temperature coefficient is greater than the effect of the oxidation and masks it so that the oxidation point can only be determined as described above. This point for zinc can be found from one measurement because of the sharp fall of potential when this temperature is exceedeed. The following data will illustrate this action and also how the change is a permanent one.

The rapid decrease shown in Part I. of these data is due to the oxidation effect minus the temperature effect and not to the sum of the two because Part II. shows that after the potential has been greatly decreased by overheating, the coefficient is still positive as for a normal zinc surface.

Erskine-Murray did not find this oxidation point because the maximum temperature he used with zinc was only 60°.

Potential Diff.	Temp.	Potential Diff.	Temp.
Part I. +.912	18.5	+.834	23.0
+.933	26.6	Part II. +.830	23.0
+.944	35.2	+.833	30.3
+.957	43.6	+.838	36.0
+.964	51.2	+.845	41.5
+.988	58.5	+.847	46.3
+.984	66.0	+.847	50.8
+.972	71.8	+.852	55.3
+.945	88.1	+.846	48.9
+.901	74.2	+.844	42.7
+.894	61.9	+.834	34.6
+.872	42.3	+.826	20.5
+.848	29.3		

For nickel, aluminum, and tin no temperature of oxidation was found up to the maximum used, 100°. Some of the observations on aluminum and tin might indicate otherwise but the lower potentials reached in these cases by cooling were only temporary effects. After standing for

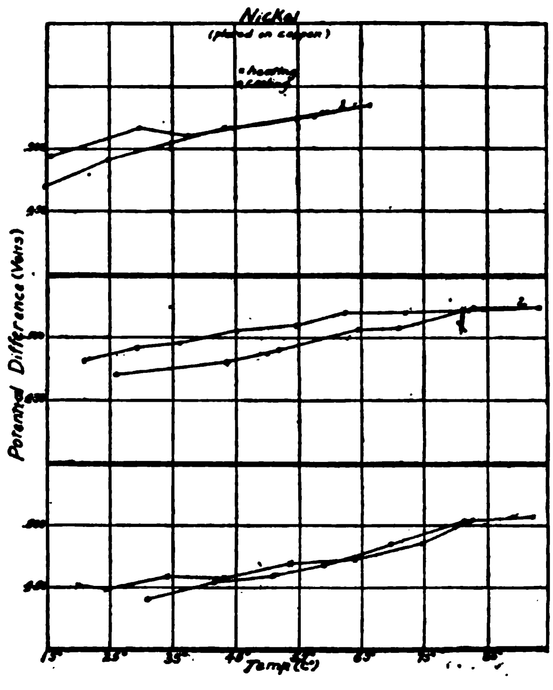

Fig. 3.

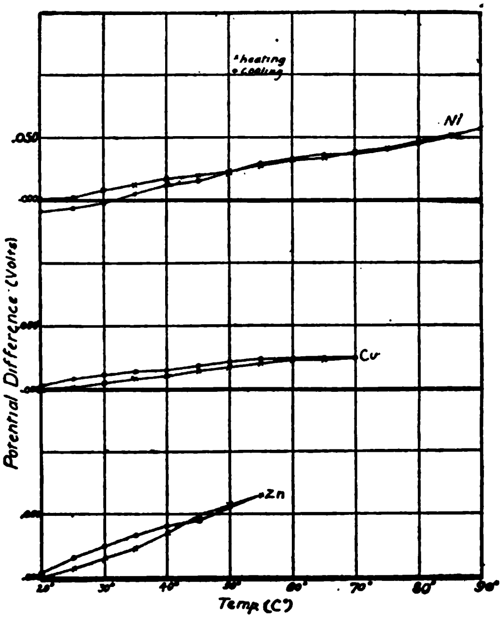
*heating
∘cooling
Ni
Cu
Zn
.050
.000
Potential Difference (Volts)
20°
30°
40°
50°
60°
70°
80°
90°
Temp. (C°)

Fig. 4.

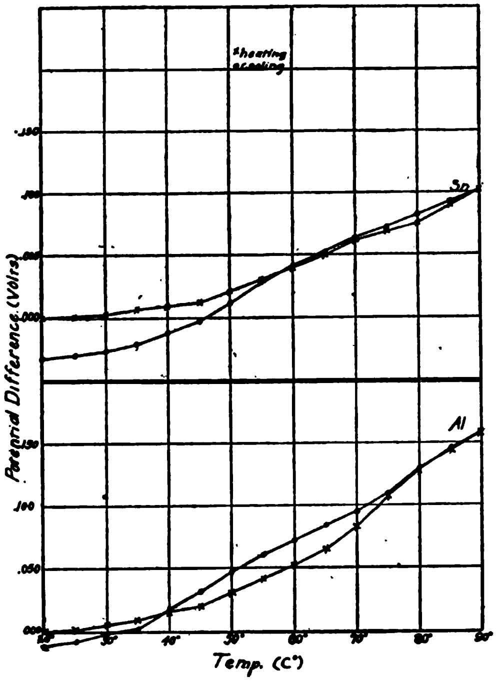
*heating
∘cooling
Sn
Al
.150
.100
.050
.000
.150
.100
.050
.000
Potential Difference (Volts)
20°
30°
40°
50°
60°
70°
80°
90°
Temp. (C°)

Fig. 5.

an hour or so the potential in each of these cases rose to, or nearly to, the value before heating. This rise in potential was not a change due to temperature because the final temperature of an experiment was usually so nearly that of the room that the hour or more standing did not change it by more than one or two tenths of a degree.

It is to be noted here that Erskine-Murray is undoubtedly mistaken in the value he gives for the coefficient of tin as he found it to be negative while the data here given show tin to have one of the largest positive values.

Curves.—Fig. 3 contains the curves showing three sets of observations on nickel. These are given as being typical in every way of the observation curves for all the metals investigated. It was curves similar to these that were used in obtaining the average curves of Figs. 4 and 5 These figures show the average change in potential with temperature without any reference to the absolute value of the potential. The average curve for nickel (Fig. 4) was obtained by taking from curve 3, Fig. 3, the potential for every 5° from 20° up to the multiple of 5° nearest to the maximum temperature used for nickel. All these values of the potential were subtracted from the value at the highest temperature and the differences tabulated. Tabulations were made in the same way from curves 1 and 2 (Fig. 3). The three differences of potential for each temperature when heating were averaged and the three when cooling separately. The value of the potential on any curve that stopped short of this highest temperature used with nickel was obtained by extrapolation except where this would exceed 5°. Finally the zero of the plot was shifted to coincide with the potential on the average heating curve at 20° temperature. This procedure amounted to shifting vertically all the observation curves for nickel until the upper extremities coincided and then getting the average of the curves so placed, with attention given only to the change in potential. A similar process was carried out for each metal giving the curves of Figs. 4 and 5. No curve of these plates is the average of less than three observation curves.

This shifting to have the maximum points coincide instead of the initial points, or some others, was done because the heating and cooling curves, of necessity, coincide at this point but do not at any other. With this choice both the average heating and the average cooling curves for a metal could be referred to the one reference point and they would coincide at that point and would appear as the curves from a single set of observations. In a case such as shown for nickel where curve 1, Fig. 3, has a much shorter range than curves 2 and 3, the mean of these two was taken down to the highest temperature on curve 1. This curve was then shifted until its extremity coincided with the mean of 2 and 3 at the same temperature. The average of the three curves was then used for the remaining lower temperatures.

Each curve of Fig. 6 is the average of the heating and cooling curves for each metal from Figs. 4 and 5. Then they are so shifted that the initial points of each resulting curve coincide with the potential which is the average of all the observed values of the difference in potential between each metal and the copper base.

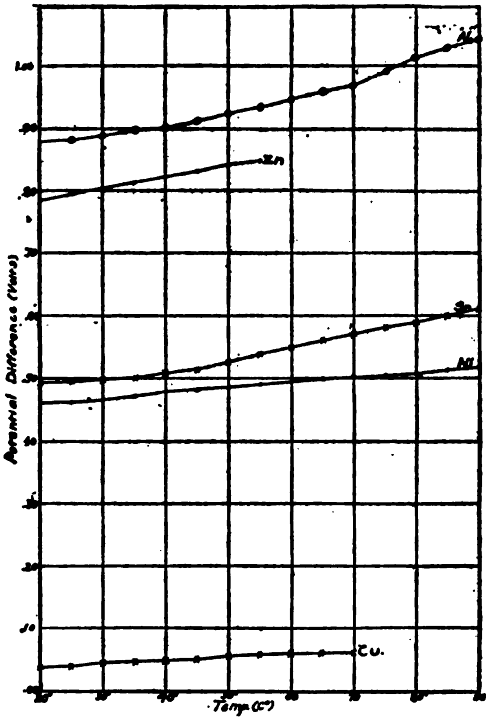

Fig. 6.

It appears that the curves for zinc, nickel, and copper are closely straight lines but those for tin and aluminum appear nearer an exponential form. The temperature coefficient for zinc, nickel, and copper is then constant over the whole range of temperature used, but for tin and aluminum it can be considered constant only for a limited range, as the numerical values below indicate.

Of course, only where the coefficient is constant would extrapolation be reasonable. Applying it to nickel, copper, and zinc, it was found that nickel and zinc would come to the same potential at – 242° (C.), copper and zinc at – 371° (C.), and copper and nickel at – 1200° (C.). Erskine-Murray states that the curves he has given would intersect at about the absolute zero if extended, though how rough an approximation this is he does not mention. The above results do not agree with his statements, that is, they do not in the least indicate that all metals would come to the same potential at the absolute zero.

Metal.	Temp. Range.	Coefficient (Volts per Degree).
Copper	20° to 70°	.00050
Nickel	20° to 90°	.00086
Zinc	20° to 55°	.0024
Tin	20° to 45°	.00096
Tin	45° to 90°	.0020
Aluminum	20° to 40°	.0011
Aluminum	40° to 70°	.0023
Aluminum	70° to 90°	.0036

It might be presumed that all the above procedure of averaging was hardly permissible considering the wide divergence of the original data, but it was done on the assumption of one or more uncertain, extraneous effects being present. If, then, these follow the law of probability, that is, that the errors they introduce are as great and as often positive as negative, then the method of obtaining the results given is justified. It is recognized that the amount of data on some of the metals was rather meager to be handled in this way, but if the assumption of extraneous effects is correct, this method would give the most probable values of the measured quantities, no matter how few the observations. It is believed that the most reasonable method of consideration was used and that the data here presented offer some dependable values of the change of contact potential difference with temperature.

It is hoped later to give further data on other metals and perhaps with a wider range of temperature and also some other aspects of the subject may be considered at that time. In conclusion I wish to thank Professor Sanford and Professor Rogers for their interest in the problem and their timely advice throughout the experimental work.

Stanford University,
May, 1913.

NOTE ON POTENTIAL ATTAINED BY PHOTO-ELECTRIC CELLS IN DARKNESS.

By J. W. Woodrow.

A FEW months ago, the present writer published in the Physical Review[1] an account of experiments which seemed to show that strongly photo-electric metals liberated positive particles when kept in total darkness. These experiments were continued with the object of determining more definitely the exact nature of the charge obtained from the photo-electric metal in the preceding investigations. It was shown conclusively by the following methods that this charge was due to a "leak" across the surface of the glass insulation, from the potassium which will be at a positive potential with respect to the platinum electrode. First, a magnetic field, sufficiently strong to deflect positive ions away from the platinum electrode, had no effect whatsoever on the observed current. Then it was found that the current could be stopped by using an amber insulation in which was inserted a platinum guard-ring which protruded both inside and outside the walls of the photo-electric cell. In the previous experiments the guard-ring employed consisted merely of strips of earthed tinfoil wrapped about the glass walls, which was thus shown to be insufficient.

The increased current at the higher temperatures is probably due to two causes, the increased conductivity of the glass and the condensation of the vapor of the metal on the walls of the cell. S. H. Anderson[2] has also shown that with alternating fields applied to a photo-electric cell in darkness, there is no indication of the current one would expect if the metal liberated any kind of positive particles.

June, 1913.

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[1] Vol. XXXV., p. 203, September, 1912.

[2] Phys. Rev., S. 2, Vol. I., p. 222, March, 1913.

THE PHOTOELECTRIC PROPERTIES AND CONTACT RESISTANCES OF THIN CATHODE FILMS.

By Otto Stuhlmann, Jr., and Karl T. Compton.

Introduction.

THE relation between the velocity of the electrons emitted by the action of light on metals and the frequency of the light was deduced by Einstein[1] on the unitary theory of light and was expressed by the equation

$$\tfrac{1}{2}mv^2 = eV = h\nu - w_0.$$

Here m is the mass, v the maximum velocity and e the charge of the electrons liberated by light of frequency ν. V is the difference of potential in electrostatic units, which is just sufficient to prevent these electrons from reaching the receiving electrode. h is Planck's constant and w_0 is the work done in the escape of an electron from the metal. Recently this same equation has been derived by Richardson[2] by thermodynamic and statistical methods which do not necessarily involve the unitary light hypothesis. Richardson's theory further enables the constant w_0 to be interpreted and calculated by the relation[3]

$$w_m - w_p = \frac{e}{300}\left\{ V_p - V_m - \theta\frac{\partial}{\partial\theta}(V_m - V_p) \right\},$$

where $w_m - w_p$ is the difference between the amounts of work required to liberate an electron from each of two metals m and p, and $V_p - V_m$ is the contact difference of potential, between the metals, expressed in volts. The last term, which expresses the Peltier effect, is so small in comparison with the contact difference of potential that it may be neglected in this work. w_0 has been measured directly for platinum[4] and for osmium[5] and is not far from $e/300\cdot 5$ volts for platinum. From this value, w_0 for any other metal may be calculated from a knowledge of their contact differences of potential.

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[1] Ann. der Physik, Vol. 17, p. 146 (1905).

[2] Phys. Rev., Vol. 34, p. 146 (1912); Phil. Mag., Vol. 23, p. 615 (1912); Science, Vol. 36, p. 57 (1912).

[3] Phil. Mag., Vol. 23, p. 620 (1912).

[4] O. W. Richardson, Phil. Trans., A, Vol. 201, p. 497 (1903); Vol. 207, p. 23 (1906). H. A. Wilson, Phil. Trans., A, Vol. 202, p. 243 (1903). F. Deininger, Ann. der Physik, Vol. 25, p. 396 (1908). O. W. Richardson and H. L. Cooke, Phil. Mag., Vol. 20, p. 173 (1910).

[5] H. L. Cooke and O. W. Richardson, Phys. Rev., Series 2, Vol. 1, p. 71 (1913).

These relations have been tested[1] for a large number of different metals and frequencies, and have been found to be consistent with the experimental results, within the probable limits of accuracy of the experimental methods employed.

Several investigators have succeeded in obtaining electron velocities considerably higher than those ordinarily obtained in photoelectric measurements. Most of these high velocities have been obtained when sparks were used as the source of light. These have been shown to be due to secondary action from electro-magnetic radiation accompanying the spark discharge. However high velocities have also been obtained in other ways. Von Baeyer and Gehrts[2] obtained velocities equivalent to 6.3 volts for electrons from copper, gold and aluminium after passing an induction coil discharge between the emitting and receiving electrodes. Recently Dike[3] has published results of experiments in which he obtained values of the maximum initial kinetic energy equivalent to as much as 44 volts for electrons liberated from thin platinum cathode films when illuminated by light from a quartz mercury arc. These results were repeated by Dike and Brown,[4] who obtained values as large as 52 volts under conditions similar to those in Dike's first experiment.

It is evident that if these results are correct they render Richardson's theory untenable. From the relation $V = 300/e \cdot (h\nu - w_0)$ discussed above, we may calculate the maximum potential possible according to the theory. 180 $\mu\mu$ is the shortest wave-length of light that will pass through the air and quartz interposed between the source of light and the illuminated metal. Take w_0 for platinum to be approximately 5 volts. Substituting these values in the above equation we find $V = 1.95$ volts. Even if the work done on an electron in escaping from the metal were zero we would still have V equal to only 9.95 volts. This is the upper limit allowed to any substance by Richardson's theory. It is an impossibly favorable case but it still falls far short of explaining the high velocities found by Dike.

It seems necessary, then, either to reject Richardson's theory or to discover some error in the results or the interpretation of the results given by Dike. It was with the purpose of discovering whether these high velocities are real or only apparent photoelectric velocities that we undertook this investigation.

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[1] Richardson and Compton, Phil. Mag., Vol. 24, p. 575 (1912); A. L. Hughes, Phil. Trans., A, Vol. 212, p. 205 (1912).

[2] Ber. d. D. Phys. Gesell., Vol. 21, p. 870 (1910).

[3] PHYS. REV., Vol. 34, p. 459 (1912).

[4] PHYS. REV., Series 2, Vol. 1, p. 254 (1913).

One of the writers[1] has shown that the velocity actually measured in photoelectric experiments consists of two parts, (1) the true initial velocity with which the electrons are liberated and (2) a velocity acquired after emission due to the force exerted on the electrons, arising from the contact difference of potential between the emitting and receiving electrodes. Of these two parts, only (1) has anything to do with the photoelectric effect and it is only this part of the measured potential which should be considered as due to photoelectric action. It seemed probable that the great increase in the photoelectric potentials following an induction coil discharge might be due principally or entirely to a great increase in the contact difference of potential. Thus the initial kinetic energy with which the electrons leave the metal film may have the ordinary value predicted by Richardson's theory. But after emission this velocity may be greatly increased by the repulsion due to an absorbed negative charge in the sputtered plate or due to their passage through a charged insulating layer, deposited on the surface by the induction coil discharge. With the object in view of testing these explanations of the apparent high velocities, these experiments were undertaken.

Apparatus.

Our apparatus, shown in Fig. 1, is essentially the same in size and arrangement as that used by Dike,[2] with the addition of an arrangement for testing the contact difference of potential between the emitting

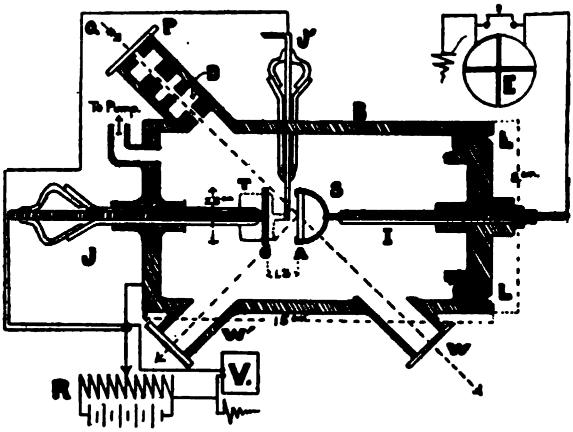

Fig. 1.

electrode and the surrounding vessel. *BB* is a cylindrical brass vessel 15 cm. long and 8 cm. in diameter. It is closed at one end by an accurately turned and ground lid, and wax could be poured into the grooves *LL* to render the vessel airtight. Through this lid extends an insulated rod *I*, which carries on its end a stirrup *S*, supporting the plate *A* on which the film under investigation is to be deposited and tested. This plate is about 2 cm. square and is connected to an electrometer *E* giving a deflection of 180 divisions per volt at a scale distance of one meter. The films were sputtered on the plate *A* from a platinum cathode *C*, which, when not in use, could be turned out of the way by rotating the ground glass joint *J* through half a revolution.

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[1] K. T. Compton, Phil. Mag., Vol. 23, p. 579 (1912).

[2] Phys. Rev., Vol. 34, p. 465 (1912).

Light from a quartz mercury arc *Q* entered the vessel through a quartz window *P* and a side tube provided with diaphragms *D*. When a quartz plate was in position at *A* the transmitted light passed out of the vessel through a window *W*, and the reflected light escaped through *W'*. In this way the reverse stream of electrons due to light incident upon the sides of the vessel was practically eliminated. The vessel could be charged to any desired potential from a potentiometer circuit *R*. The maximum initial kinetic energies of the electrons, expressed in equivalent volts, were determined by charging the vessel to such a negative potential that the electrometer showed no deflection. The voltmeter *V* then gave the maximum potential directly. By this *null* method we avoided possible errors due to faulty insulation. When saturation currents were to be measured, the vessel was charged to a sufficiently high positive potential and the rate of deflection of the electrometer noted.

As pointed out above, it is necessary to apply a correction for contact difference of potential to the measured values of the maximum potential in order to find the true photoelecrtic potentials. This contact difference of potential between the metal film on *A* and the vessel *BB* was determined by the Kelvin method.[1] The contact difference of potential tester *T* consisted of a brass plate, of the same dimensions as the plate *A*, fixed on a movable arm to the end of a brass rod which extended to the outside of the vessel through the ground glass joint *J'*. By rotating this joint the test plate could be moved close to *A* or back against the side of the vessel. The tester *T* was raised to various potentials from the divided circuit *R*, and the potential was so adjusted that no kick of the electrometer was produced by moving *T* back and forth in front of *A*. The voltmeter, under these conditions, gave a direct measure of the contact difference of potential between *T* and *A*. An objection to this arrangement is that it measures the contact difference of potential between the emitting electrode and *only a particular part* of the receiving electrode. If the inside of the vessel always remains a polished brass surface this arrangement would introduce no error. However, if the induction coil discharge, during the process of sputtering, changes the condition of the inside surface of the vessel and changes it more in some regions than in others, the above method will not be accurate, because it is not certain that the contact difference of potential actually measured is the true difference of potential between the emitting electrode and that portion of the vessel to which most of the electrons are escaping. Nevertheless, if any considerable changes in the contact difference of potential occur, this method should give at least an approximate measure of these changes. For this reason the contact potential measurements should be considered as indications of what surface changes are produced by the electrical discharge rather than as accurate quantitative measures of these changes. It will be seen, however, that these indications are fairly accurate, especially in the case of the larger effects measured.

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[1] Kelvin, Phil. Mag., Vol. 56, p. 82 (1898).

The sputtering was all done at a pressure of $(10)^{-4}$ cm. of mercury by means of the discharge from a small induction coil capable of giving a spark of about 4 cm. in air. The thickness of the deposited film may be taken to be proportional to the time of sputtering. The photoelectric measurements were all made at a pressure of $5(10)^{-6}$ cm. or less.

Effect of Reflected Electrons.

A number of investigators[1] have assumed that electronic reflection at the receiving electrode causes a reverse stream of electrons which reduces the measured value of the maximum acquired photoelectric potential. Dike and Brown[2] offered this as one of the possible reasons for the high potentials obtained in their experiments. They further suggested that Robinson,[3] who also worked with sputtered films, did not obtain high velocities like they did because the construction of his apparatus may have made a difference in the amount of electronic reflection. It is hard to see, however, how electron reflection can have any effect on the maximum photoelectric potential. Suppose that fifty per cent. of the fastest electrons which strike the receiving electrode are reflected and return to the plate from which they started. This will not prevent the electrode from charging to the same maximum potential which it would attain were there no reflection. Under these conditions the final potential will be attained just half as rapidly, but it is inconceivable that the final potential will be altered. Especially is this true when the maximum potential is measured by a *null* method which eliminates errors due to imperfect insulation. Electronic reflection certainly must be prevented in case "distribution of velocity" curves are to be obtained, but its influence may be neglected in measurements of maximum potentials or of saturation currents. The apparent increase in the maximum potentials when electron reflection has been reduced by a perforated gauze and an auxiliary field has been shown to be a spurious effect.[1] For these reasons we have, in these measurements, made no effort to measure or prevent electronic reflection.

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[1] Ladenburg and Markau, Verh. d. D. Phys. Ges., p. 562 (1908); Von Baeyer and Gehrts, loc. cit.; Klages, Ann. der Phys., Vol. 31, p. 343 (1910).

[2] Phys. Rev., Series 2, Vol. 1, p. 254 (1913).

[3] Phil. Mag., Vol. 23, p. 542 (1912).

ORDINARY PHOTOELECTRIC POTENTIALS.

(*a*) *No Evidence of Absorbed Charge.*—In our first trials the cathode films were deposited on quartz in a separate sputtering vessel, which consisted of a large glass bell-jar waxed on a brass base plate, with the electrodes sealed in. The contact difference of potential was then tested in air by the ionization method,[2] which is more accurate than the Kelvin method but which may only be used while the films are in contact with the air. Then the sputtered plate was placed in position in the apparatus, the vessel exhausted and the maximum photoelectric potential measured. This process was repeated for three films of different thicknesses. The results are shown in Table I.

TABLE I.

Potential.	Platinum Film.		
	Very Thin.	Medium.	Thick.
Maximum	1.45 volts	1.65 volts	1.85 volts
Contact	−0.15	−0.15	−0.15
Corrected	1.30	1.50	1.70

Evidently this method does not yield the high potentials found by other investigators. On the other hand these maximum potentials are of the order of magnitude predicted by Richardson's theory. While the potential apparently is higher for the thicker films, the differences are small and may be due to experimental error, since the apparatus is not well designed for measuring potentials accurately to a fraction of a volt.

The results are, however, of some interest. The contact differences of potential are practically identical with that between brass and ordinary platinum. The photoelectric potentials are also what one might expect from platinum foil. It is quite certain, therefore, that these films consist of true platinum. The photoelectric potentials showed a tendency to increase slightly with time, the increase amounting to one or two tenths of a volt in several hours. This "aging" effect has been noticed before by Dike and by one of the writers.[1] The saturation currents were larger than those usually obtained from platinum. This was true for all the sputtered films investigated. An important result bearing on the problem under investigation is that the induction coil discharge evidently produces no "absorbed" charge in the quartz. Hence the high potentials obtained by Dike cannot be ascribed to this cause. An absorbed charge in the quartz, if it existed, would not have vanished immediately on contact with the air and would have been easily detected by the contact difference of potential measurements.

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[1] Compton, Phil. Mag., Vol. 23, p. 277 (1912).

[2] Kelvin, Beattie and Smolan, Phil. Mag., Vol. 45, p. 277 (1898).

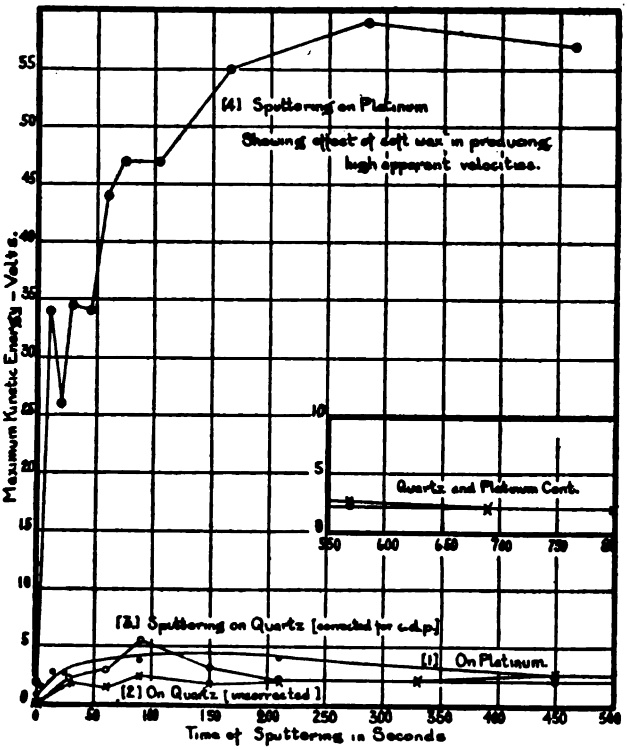

Fig. 2.

(*b*) *Films Sputtered and Investigated in Vacuo.*—Films sputtered on quartz and on platinum foil in the apparatus (Fig. 1) were tested for contact difference of potential and for photoelectric potentials and saturation currents without allowing the films to come in contact with the air.

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[1] Stuhlmann, Phys. Rev., Series 2, Vol. 4, p. 330 (1913).

Results as shown in Fig. 2, curves 1, 2 and 3, were obtained. Curve 1 represents the variation of maximum potential with the time of sputtering, for films sputtered on a platinum plate. The highest measured potential is 3.9 volts. Since the contact difference of potential remained too small to be detected accurately by the Kelvin method no corrections for contact difference of potential were made. Curve 2 represents the photoelectric potentials for various thicknesses of films deposited on quartz. In this case the contact differences of potential were measurable and the corrected potentials are shown in curve 3.

Several facts are evident from these results. The potentials were rather irregular, most of the irregularities occurring in the early stages of sputtering. The contact differences of potential also varied, and further experiments showed that they varied also in different parts of the vessel. These photoelectric potentials are distinctly higher than those for ordinary platinum, although they still fall far short of those obtained by Dike and Brown.[1] Since the following experiment throws light on these results they will not be discussed further at this point.

SPURIOUS HIGH PHOTOELECTRIC POTENTIALS.

Up to this point it appeared that, although we had followed closely the method used by Dike, we were unable to duplicate his high velocities. Following a suggestion from Professor Richardson, however, we made another trial and succeeded in obtaining the high potentials, even exceeding the highest values obtained by either Dike or Brown.

TABLE II.

Time Sputtered.	Contact Potential.	Photoelectric Potential.
0 sec.	− 0.1 volt	1.8 volt
10	−16	35
10	−22	26
10	−28	34.5
15	−28	34
15	−37	44
15	−40.5	47
30	−40	47
60	−57	55
120	−57	59
180	−57	57

A tiny bit of soft wax was placed on the sputtering cathode and the above experiments were repeated. From the first the measured potentials were high, and are here shown graphically in Fig. 2, curve 4. After a film due to five minutes of sputtering had been deposited the corresponding maximum observed potential had risen to 59 volts. Further sputtering did not increase this value.

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[1] Loc. cit.

That these high potentials do not indicate high photoelectric velocities is shown by the fact that the contact difference of potential between the film and the vessel increased parallel with the photoelectric potential, in such a direction as to make the emitting film electro-negative and repel the electrons after they were emitted. The parallelism between these quantities is shown in Table II.

This enormous contact difference of potential is not the true contact difference of potential between the film and the chamber of the apparatus. If these high values represented true contact differences of potential, no photoelectric effect would be possible with light of the frequency used, since under these conditions $h\nu$ would be smaller than w_0. The effect is evidently due to a charged layer of soft wax covering the platinum film, within which layer the escaping electrons experience an enormous acceleration. This charged layer persisted for about 24 hours after air had been let into the apparatus. During this time the apparent contact difference of potential gradually fell to its normal value of − 0.15 volt. The saturation currents under these conditions were a little more than half as large as in the similar tests where the soft wax had been omitted. This again gives evidence of some sort of layer through which the electrons were obliged to pass while escaping.

It is evident from these results that the high potentials observed by Dike and later also by Dike and Brown must be ascribed to the presence of oil or grease introduced while making the metal apparatus, to vacuum wax in the ground joints or to some other material which could produce such layers as suggested. Doubtless the small increase in potential which we observed before we intentionally introduced the soft wax was due to wax or grease unavoidably present in any form of metal apparatus.

There is therefore no evidence in these experiments to show that the photoelectric velocities should be different from those predicted by Richardson's theory. There are certain theoretical reasons for believing in the possibility of small variations in the saturation currents and maximum potentials from very thin films; but these effects, if they exist, will probably not exceed a fraction of a volt and will be taken into account by a variation in the quantity w_0 for very thin films.

Saturation Currents and Contact Resistances.

Several interesting phenomena are exhibited by the relations between saturation photoelectric currents and thickness of films, which are shown graphically in Fig. 3.

One of the most striking things about these curves is the influence of the nature of the contacts on the shape of the curves. In curve 5 the film was deposited directly on a platinum plate. The saturation curve under these conditions is a smooth curve of logarithmic form. Contact between the sputtered film and the platinum plate was evidently established from the very beginning, as is indicated by the lack of certain characteristic phenomena which appear in all curves for saturation currents from films sputtered on glass or quartz. In curve 7 the contact between the sputtered film and the supporting stirrup was made as follows. A thick opaque platinum film was first sputtered on the quartz and a central strip was removed, leaving two strips of film about 3 mm. wide on the two opposite edges. The clamps of the stirrup were now fastened to these edgings and the films to be investigated were sputtered over this prepared surface. This was done with the idea in view that the film to be deposited would spread in a uniform layer over the cleaned quartz and the sputtered contacts alike, and in this way the preliminary film would serve as an intermediate contact between the sputtered film and the contact clamp. It is evident in this case that contact was not perfect from the beginning as in the case of curve 5, and that no contact with the film was established until the sputtering had continued about 25 seconds.

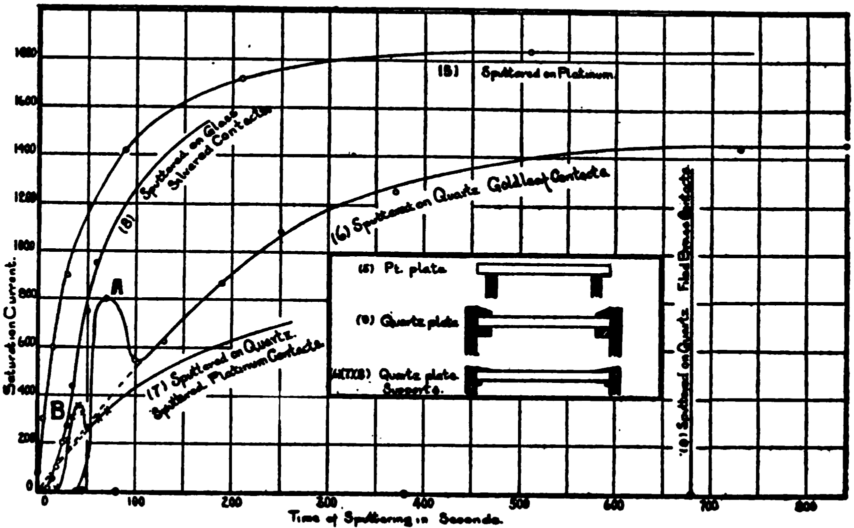

Fig. 3.

To show that the absence of photoelectric currents in the early stages of sputtering is really due to the absence of electrical contact rather than to some inherent photoelectric property of very thin films, various other methods of making contact were employed. These methods, with their differences greatly exaggerated, are shown in Fig. 3. For curve 6 we used gold leaf contacts. Strips of gold leaf were placed firmly adhering to the two opposite edges of the quartz plate and the contacts were clamped down on this leaf. In this case the discontinuity of surface between the quartz and the gold leaf would be more pronounced than between the quartz and the sputtered film used previously. The preliminary film used for contact in the case of curve 7 was much thinner than the gold leaf and therefore a less abrupt discontinuity was found between the film under investigation and the contacts. As might be expected, the contact in this case was more difficult to establish, and was not obtained until the sputtering had continued for about 55 seconds.

A still greater degree of difficulty in establishing contact between film and holder is shown by curve 9. In this case a clean quartz plate was simply held in a brass clamp whose edges had been filed down to a very sharp angle, whose vertex rested flush on the quartz plate. The bounding surface was much more abrupt in this case than in the others. This time sputtering continued for at least 680 seconds before contact was made and currents obtained from the film. In fact this film was of such a thickness as to be quite opaque.

It is evidently a very difficult matter to make good electrical contact with very thin films. The less abrupt the boundary between the surface of the contact film or plate and the quartz surface on which the film is deposited, the more perfect will be the contact. At first sight it may seem unlikely that a contact edge as thin as gold leaf would prevent uniform deposition and perfect contact with the film. But when one remembers that these thinnest films are many times thinner than a wave-length of light, it is easy to believe that the deposited molecules must "bank up," so to speak, at the edge of the contact before continuity is obtained.

There are two applications of this experiment on the effect of the method of making contact with the films, to which we would call attention. In the first place it explains why, in our results and also in the recent results of Robinson,[1] little or no photoelectric current was observed until the film had reached a certain thickness, where the current showed a sudden increase. The above results seem to show that this is due to imperfect contact rather than to any inherent property of very thin films.

It also offers a possible explanation of some of the results obtained by

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[1] Phil. Mag., Vol. 25, p. 115 (1913).

Patterson[1] on the specific resistance of thin metal films. He found for very thin platinum films that the specific resistance increased more rapidly than was predicted by the electron theory of conduction suggested by J. J. Thomson.[2] It seems possible that all or part of this unpredicted increase may be due to high contact resistance superposed on the regular resistance of the film. If this is true it would explain the discrepancy between theory and experiment in the case of very thin films. We also tested photoelectrically a film with contacts very similar to those used by Patterson, with the results shown in curve 8. The contact between film and holder was here established by sputtering the platinum film over a quartz plate whose two opposite edges had been covered by means of a semitransparent silver film, deposited by the Rochelle salt method. This method of establishing electrical contact between film and holder was evidently the most perfect yet tried. As seen from the curve, contact was established soon after 10 seconds' deposition. Had contact been made from the first it is probable that the resistance which Patterson measured would have been found to conform more closely to the theory discussed in his paper.

[1] Phil. Mag., Vol. 4, p. 652 (1902).

[2] Proc. Camb. Phil. Soc., Vol. 11, 2, p. 119 (1901).

VECTOR POTENTIAL IN RELATION TO VECTOR ANGLE

By Frederick Slate.

THE recent freer use of the various potentials has not carried with it their adoption as quantities that are physical in the fullest sense of the word; they continue to be set off somewhat as "Rechnungsgrössen"—formal aids to calculation or summarized expression, employed without always searching deep for possible physical significance. It is true that the oldest potential, the scalar potential of gravitation, electric charges and magnets, has recognized connections with energy, familiar enough in fact to guide the conventions standardizing its sign and magnitude. But the vector potential, its chief companion, is still more enveloped in mathematical haze than is desirable; its physical aspects are obscured by its association with certain operations and theorems whose mystery is not yet dissipated. As a mode of statement within modern electromagnetic theory, however, accepted finally, it would appear, after some protest against its inadequacy or superfluousness, the vector potential will be engaging increased attention. It should be properly strengthened by whatever of direct physical meaning we can gather round it, and what follows here is a small contribution to that general end, taking up a clew offered through the vector algebra, which enables us to read a new sense into the parallelism between the scalar and the vector potential, to the advantage of the latter, rated as a physical concept.

First as to the geometrical and preparatory ideas, that happen to be connected with solid angle. Assuming a pole (P) let the extremity of a radius vector ($\mathbf{r}$) be guided along any closed curve (s) in space, tracing in general some conical mantle, whose surface we may suppose not to cut itself, in order to avoid mere complication in details. Then the differential tangent-sectors give instantaneously the resultant elements of plane angle described by the radius vector, the aggregate of angle being a vector sum. This appears in the form

$$d\mathbf{a}_1 = \frac{1}{r^2}[\mathbf{r}d\mathbf{s}]; \int d\mathbf{a}_1 = \int_s \frac{1}{r^2}[\mathbf{r}d\mathbf{s}], \qquad (1)$$

which includes the particular case where the guide-curve (s) lies all in one plane that contains the pole (P) also.[1] The sphere of unit radius

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[1] Slate, Phys. Rev., N. S., *1*, p. 56.

(unit sphere) centered at the pole determines by its intersection with the conical mantle the boundary (s_1) of the solid angle subtended by the curve (s) at the point (P), if we accept the area of the spherical cap ($r = 1$) as the measure of that solid angle.[1] Then by a simple continuation we write the vector expression for an areal element on the unit sphere, in the strip bordered by the curve (s_1) whose width is determined by a second coördinate ($d\mathbf{s}_2$),

$$dS_1 = [d\mathbf{s}_1 d\mathbf{s}_2] = [d\mathbf{a}_1 d\mathbf{a}_2]. \qquad (2)$$

The third member of this equation can be read in two ways, according to the form of the thought attached to the second member. First, in terms of angle-area, the third member multiplies axial vectors; perpendiculars to the linear vectors multiplied in the second member, but numerically equal, each to each. The second factor ($d\mathbf{a}_2$) is the angle for the center (P) corresponding to the arc ($d\mathbf{s}_2$). The product, being of necessity oriented in the radius vector, is evidently unchanged by turning both factors through any common angle about that line. But secondly, the factors in the third member are only synonyms for those in the second, if we can adopt the arc-element of the unit circle to represent angle (*i. e.*, by a linear vector in the plane of the angle).[2] Either point of view enables us to look upon solid angle as generated by an integrated double movement in plane angle of the radius vector, a scalar sum being formed finally of the elements of area whose normals are all radial. And since the cap has been taken on the unit sphere, these results again are entirely consistent with a connection of solid angle and volume, through the expression[3]

$$A = \int_S \frac{1}{r^3}(\mathbf{r}dS). \qquad (3)$$

Further, as a closing word on the geometrical relations, we may note that the sector of the unit sphere determined by the curve (s_1) being bounded by a closed surface, the projections on any plane of its conical mantle and of its spherical cap must be equal magnitudes, but subject in sign, of course, to the established rule of "outward normal." This conclusion has an evident extension to any distribution of physical vector that is homogeneously proportional to area throughout mantle and cap.[1]

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[1] Following Maxwell's definition, El. and Mag., *2*, p. 39. A double or triple line of specification, whose equivalences rest finally upon certain coincidences of value for unit radius, is found current and supported by good authority through the whole group of angular quantities. There seems to be no ground in logic for adhering exclusively to one plan and ignoring special conveniences; and any necessary reassignment of dimensions can be taken account of easily. This freedom of choice among alternatives is made use of later.

[2] This presentation of angle as arc-element is not complete in vector algebra, it is clear, unless somehow supplemented by knowledge of the angle's plane; here, *e. g.*, through location of the center (P). This measure of angle underlies the specification of angular velocity as cm./sec. (explicit in Klein and Sommerfeld, Kreiseltheorie, p. 11). Such instances remind us that a vector quantity may be treated on more conventional bases than one; with "no questions asked" about pedigree.

[3] Slate, loc. cit., p. 57.

Passing now to physical application of what precedes, as a matter of greater present concern, the most essential points can be brought out if we consider the simplest case: The curve (s) is a rigid conducting circuit carrying stationary current, and a positive magnet-pole is at the point (P). The inclusion of displacement current; and of conditions that introduce retarded potentials; can be shown without difficulty to demand no fundamental modifications. Reckoning then for unit of current and of pole strength (and we will add unit of permeability), the resultant interaction between the pole and a current-element in the direction ($d\mathbf{s}$) at an angle (ϑ) with the radius vector (r) drawn from the point (P), is given correctly by

$$d\mathbf{F}_1 = \pm \frac{1}{r^3}[\mathbf{r}d\mathbf{s}]. \tag{4}$$

For our purpose the relations depend upon configuration, and we may regard the pole as fixed, while the circuit suffers translational displacement. The element of force-moment for origin at (P), active on the element of circuit, is

$$d\mathbf{M}_1 = \left[\mathbf{r}, -\frac{1}{r^3}[\mathbf{r}d\mathbf{s}]\right] = d\mathbf{s}_1 = \frac{ds}{r}\sin\vartheta \left\{ \begin{array}{l} \text{perpendicular to } r \\ \text{in the plane } (r, ds) \end{array} \right\}. \tag{5}$$

The directed elements of the curve (s_1) on the unit sphere gain thus a new special meaning, adaptable to any general values for current and pole-strength by the introduction of a proper tensor as factor, which we shall continue here, however, to treat as unity. Moreover, our value for the element of force-moment about an axis at (P) drawn parallel to ($d\mathbf{s}_1$) exhibits to inspection a maximum (all other conditions remaining unaltered),

$$d\mathbf{M}_1(\text{max.}) \equiv d\mathbf{M} = \frac{1}{r}d\mathbf{s}\left[\text{for the direction } \vartheta = \frac{\pi}{2}\right]. \tag{6}$$

And the form of the expression in eq. (5) opens the way to consider this maximum (oriented parallel to ($d\mathbf{s}$)) as a resultant, in the sense that its projection upon the actual axis yields the force-moment available about that axis. Therefore specially, assuming reference axes at the origin (P) and using the direction-cosines (l, m, n) of ($d\mathbf{s}$), we derive for moments available about (X, Y, Z):

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[1] Compare Maxwell, El. and Mag., 2, pp. 29–44, as a classic reference, needing only to be "popularized" by translation into simpler modern forms, and by some reading between the lines.

$$dM_x = \frac{l}{r}\,ds;\ dM_y = \frac{m}{r}\,ds;\ dM_z = \frac{n}{r}\,ds. \tag{7}$$

Let now the circuit (s) be shifted by translation, causing angular displacement ($d\mathbf{a}$) of the radius vector drawn to ($d\mathbf{s}$), and the doing of work by the force-moment ($d\mathbf{M}_1$) to the amount

$$dW = (d\mathbf{M}_1 d\mathbf{a}) = d\mathbf{M}_1 d\mathbf{a}' = (d\mathbf{M} d\mathbf{a}'). \tag{8}$$

The factor ($d\mathbf{a}'$) is the effective angular displacement; namely the component colinear with the total force-moment ($d\mathbf{M}_1$) of eq. (5). Hence we may read equations (7) and (8) in these terms:

The maximum force-moment ($d\mathbf{M}$) gives by a definite plan of projection upon any line through the origin the work per unit angle (or also the work reckoned for unit angle) of displacement about that line as axis. And these alternatives are dimensionally equivalent, when angle is a numerical quantity.

And further, returning to eq. (2), since the factors ($d\mathbf{s}_1$) and ($d\mathbf{a}_2$) are colinear when the width ($d\mathbf{s}_2$) is perpendicular to ($d\mathbf{s}_1$) and we are dealing with angle-area, the scalar product in eq. (8) is the numerical equivalent of the vector product in eq. (2); and on comparing we can see how the work done locally by the active moment comes to be measurable by an increment (dS_1) of solid angle at an element of the boundary (s_1).

But it may be desirable to think of the pole as displaceable and the circuit as fixed; and this transition offers no difficulty. For just as both aspects of an interaction in the junction-line of two active elements are comprehended in one concept of stress, so an interaction of the present type that is perpendicular to the line joining the active elements may be viewed inclusively as one couple, whose moment-vector accordingly may be drawn indifferently at either end of the radius vector. And the same work-element also is determined from each point of view, because the angular displacement retains sign and magnitude, when adjusted to the equivalent linear displacements of pole and circuit, which must be opposite as well as equal.

The attention given thus far to the differential element only of the interaction between circuit and pole does in fact reveal all the essentials of the situation. But it remains necessary to express the result of summing effects by taking account of the whole group of elements in the circuit (s). We can execute this conveniently by forming from eq. (7) the algebraic integrals

$$M_x = \int_s \frac{l}{r}\,ds;\; M_y = \int_s \frac{m}{r}\,ds;\; M_z = \int_s \frac{n}{r}\,ds. \tag{9}$$

These expressions for its components enable us to recognize the quantity $\boldsymbol{M} = \boldsymbol{M}_x + \boldsymbol{M}_y + \boldsymbol{M}_z$ as the vector potential at the point (P); and the same identification is deduced from eq. (6), if we write for the vector sum and its components[1]

$$\boldsymbol{M} = \int_s d\boldsymbol{M};\; M_x = M\cos\alpha;\; M_y = M\cos\beta;\; M_z = M\cos\gamma. \tag{10}$$

It is apparent that no important difference exists between the two statements; only an interchanged order of the operations: (1) Projection; and (2) summation; plainly justified by the fundamental equivalence of resultant and its group of components as affected by the same operator. We shall note this legitimate inversion in another connection presently. The main result of our discussion might then be summarized at this stage in a definition of vector potential as a single-valued vector point-function, whose local value is determined in direction and magnitude by the total at each point of the force-moments due to other active material in the field, and described in the italics following eq. (8). We are thus put in a position to anticipate the reason why the vector potential presents itself as a convenience, where (and wherever) the field-forces, though (1) functions of the relative coördinates only, are (2) perpendicular to junction-lines and not directed along them; and how the scalar and the vector potential are supplementary in the dynamics of force-fields; primarily, we may say, as regards the types of interaction to which they apply naturally, for their equality in dimensions (those of energy) is on the surface formal and will not lead far. Nevertheless, the formulation in the above terms suggests on another side a comparison of the vector potential with the vector parameter (gradient) of the scalar potential rather than direct association of the potentials themselves. For the gradient may be specified in complete parallel, by substituting the element of (radial) force for the element of force-moment in the vector potential. That is, with inversion of the more habitual process, just quoted as allowable, the gradient too can be obtained by assembling the projections of a group of elementary force-maxima. Pairing in the way indicated, the distribution of forcive throughout the field can be traced; the local value of the vector potential yields force-moment, and that of the gradient yields force; in both cases alike by the one operation of projection. It is equally true, however, as another unconstrained reading of what precedes, that the force-moment about any line is obtainable by a process akin to "axial differentiation" with respect to vector-angle applied to the vector potential; leading here to the same result as mere projection because this particular differentiation leaves dimensions unaltered when angle is a ratio.

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[1] Eq. (9) is the plain equivalent of Maxwell, El. and Mag., 2, p. 44, eq. (9); while his construction (p. 44, foot) can be based directly upon our eq. (10), which is also (for unit of current) the vector form found in the literature of electromagnetism. It is worth remarking that this type of line-integral shows the aggregate effect of some actual and limited distribution *in situ;* for instance, the total weight of a curved rope, not uniform in cross-section. To repeat such a summation would be meaningless, whereas a progressive displacement round a closed curve is capable of repetition, and may give through a line-integral work corresponding to a multiple-valued potential. Observe further that the integrals of eq. (9) may possibly vanish as moments, though the summed work of the moment-elements does not become zero. This is a counterpart of the fact that a couple (which is zero force) may contribute a finite amount of work.

If the vector potential gives one method of expressing work, known to be energetically equivalent to a second method where the scalar potential is used, the same amount of work for any given displacement becomes calculable in terms of force-moment exerted during a turning and also in terms of linear displacement under a straight pull. The familiar connection between a current-circuit and a properly chosen magnetic shell is readily deducible on the basis of eq. (8), the values of the potentials being harmonized by taking the conventional zero at infinity for both. But we must expect that an attempt to develop complete symmetry in the operations applied to the two potentials and their results will be disturbed by obstacles. For example, the imperfect balance of cross relations between forces and couples prevents a match to the partial determination of moment by the former with a contribution to force by the latter; couple-moments are free vectors while a force vector may be localized in its "line of action." Again the junction-line of two active elements is unique, but a coördinate perpendicular to such a line needs further definition. Consequently, when a derivative of the vector potential is connected with a force perpendicular to the coördinate used in forming the derivative, the particular perpendicular is in fact also specified. This is perhaps the closest analysis of the necessary vector quality in this potential; and it underlies as well the occurrence here of the curl operator, as causing "quadrantal advance" in direction for the derivatives that enter.

UNIVERSITY OF CALIFORNIA.

THERMAL AND ELECTRICAL CONDUCTIVITIES OF THE ALKALI METALS.

By J. W. Hornbeck.

I. Introduction.

ONE of the first successes of the modern electron theory consisted in its very simple explanation of the constant ratio of the thermal and electrical conductivities for the metallic elements. However, a closer study of the conduction of heat and electricity through metals, of their thermo-electric and magnetic properties, showed that the simple theory, which considered the electrons to move freely through the metal, was unable to explain the manifold and complicated phenomena in a satisfactory way.

It was first assumed, in the theories of Riecke, Drude, J. J. Thomson and H. A. Lorentz, that the electrons are free and share the heat motion of the atoms; but this assumption leads to a number of contradictions. When one determines N, the number of free electrons per cubic centimeter, by the method of the conductivities for heat and electricity for the different metals, values are found which differ greatly[1] from those derived from the Peltier effect. Moreover, the experiments of Rubens and Hagen show that the electrical conductivity of metals for alternating currents of very high frequency remains practically the same as for steady forces, and the values of N which follow from these data are impossible[1] in view of the known values of the specific heat. Furthermore, Lees[2] measured the thermal and electrical conductivities of a number of metals down to the temperature of liquid air and found an increasing deviation from the law

$$\frac{\lambda}{\sigma} = \frac{4}{3}\frac{\alpha^2}{e^2}T.$$

A change in structure has a large effect on the thermal and electrical conductivities. For instance it has been found recently[3] that the resistance of mercury at 4.2° absolute drops suddenly from 0.11 to zero. Small impurities have large effects. Metals and alloys often behave in opposite ways. For example, the heat conductivity of the metals decreases slightly with increasing temperature, while for the alloys it increases with the temperature. Moreover, the ratio $\lambda/\sigma T$ increases slightly between $-180°$ C. and $+20°$ C. for the metals, and decreases considerably for the alloys.

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[1] J. J. Thomson, Corpuscular Theory of Matter, pp. 76, 84.

[2] C. H. Lees, Phil. Tran., Royal Soc., Vol. 208, p. 381, 1908.

[3] H. Kamerlingh Onnes, Com. Phys. Lab. of Univ. of Leiden, No. 124, p. 23.

These facts cannot be explained by the present theories even when it is assumed, as Lorentz and Richardson[1] have done, that the distribution of the velocities of the electrons is that which corresponds to Maxwell's expression.

The strongest evidence against this conception of the electric current consists in the fact, shown by Nernst, that the specific heat of metals approaches zero as the temperature approaches the absolute zero. If the current were due to the motion of free electrons which are in temperature equilibrium with the metal, then the specific heat would be due mainly to the free electrons and would therefore, as in a gas, change very little with decreasing temperature. The question arises as to whether the electrons carrying the current take part in the specific heat.

Several modifications of the original theory have been proposed, but none of them gives an adequate quantitative explanation of all the phenomena. The various theories agree only in the fundamental assumption that the current is carried by electrons. This is in harmony with the general facts that the good conductors are metals, positive elements, ready to part with a negative electron; that the metals when struck by ultra-violet light or Roentgen rays, or when heated to a certain temperature, emit electrons; and that the current in the metals shows the Hall effect.

The decrease of the specific heat with decreasing temperature is at least qualitatively accounted for by Planck's theory of radiation. It is possible that the electrons have at low temperature no part in the specific heat of the metals, so that the specific heat is entirely due to the motion of the atoms or to their elementary oscillators. According to this conception there are no free electrons at all, at least at low temperatures, and the electrons escape only when they have acquired a sufficient amount of kinetic energy to overcome the attraction of the positive "rest-atom." Then there should be a definite relation between the energy of the electron and the energy of the atom.

We shall assume that the electrons part with the atom when their kinetic energy is proportional to the energy E of the atom. Moreover, for the energy of the atom, or the oscillator in the atom, we shall assume the expression given by Planck[2]

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[1] Planck, Acht Vorlesungen über Theoretische Physik.

[2] O. W. Richardson, Trans. Am. Chem. Soc., Vol. XXI., 1912.

$$E = \frac{hn}{e^{\frac{hn}{kT}} - 1},$$

or, according to the modified theory,

$$E = \frac{hn}{e^{\frac{hn}{kT}} - 1} + \frac{hn}{2}.$$

Then the kinetic energy of the electron is given by

$$E_1 = \tfrac{1}{2}mv^2 = \gamma \frac{hn}{e^{\frac{hn}{kT}} - 1},$$

where γ is some constant, and from this equation we know v as a function of T. The constant term $hn/2$ has no effect in the present application of the Planck theory. If l is the mean free path and t the time during which the electron moves from one atom to the other, then

$$v = \frac{l}{t}.$$

The force acting on the electron in the field E' is $E'e$, and the acceleration

$$a = \frac{E'e}{m}.$$

The mean time during which this force acts is $t/2$ seconds and hence the field superposes a velocity

$$u = \frac{at}{2} = \frac{E'el}{2mv}.$$

The number of electrons passing through unit cross-section per unit time is

$$Nu = \frac{NE'el}{2mv},$$

and the current density

$$i = Nue = \frac{E'e^2Nlv}{2mv^2} = \sigma E'.$$

Whence

$$\sigma = \frac{e^2Nlv}{2mv^2} = \frac{Nlve^2}{4E_1} = \frac{Nlve^2.}{4\gamma \frac{hn}{e^{\frac{hn}{kT}} - 1}}. \tag{1}$$

For the quantity of heat energy passing through unit area per unit time, we have

$$H = \frac{1}{3} Nvl \frac{\partial E_1}{\partial x} = \frac{1}{3} Nvl \frac{dE_1}{dT} \frac{dT}{dx} = \lambda \frac{dT}{dx}.$$

And

$$\lambda = \frac{1}{3} Nvl \frac{dE_1}{dT}. \tag{2}$$

Hence

$$\frac{\lambda}{\sigma} = \frac{4}{3e^2} \frac{dE_1}{dT} E_1. \tag{3}$$

Substituting in (3) the values of E_1 and dE_1/dT, we have

$$\frac{\lambda}{\sigma T} = \frac{4}{3} \frac{\gamma^2 h^3 n^3}{e^2 k} \frac{1}{T^3} \frac{e^{\frac{hn}{kT}}}{\left(e^{\frac{hn}{kT}} - 1\right)^3}. \tag{4}$$

If hn/kT is small, we can expand the exponential functions and equation (4) for the higher temperatures assumes the form

$$\frac{\lambda}{\sigma T} = \frac{4}{3} \gamma^2 \frac{k^2}{e^2} \left(1 - \frac{hn}{2kT}\right). \tag{5}$$

As T increases, according to equation (5), the values of $\lambda/\sigma T$ should approach a constant value and this agrees with the facts. Moreover, when the values of $\lambda/\sigma T$ are plotted against T in equation (4), the curve is found to be of the same form as the experimental curves which Lees obtained for the pure metals at low temperatures. Thus we have a formula which explains the behavior of $\lambda/\sigma T$ for pure metals and which also leads approximately to the right expression for the variation of the specific heat with the temperature. It agrees with Einstein's formula for specific heat; in fact, both formulæ rest upon Planck's expression for E.

It is not claimed that this theory is complete. It is merely suggested as a possible step in the right direction because it removes two important difficulties of the electron theory without introducing new contradictions. The phenomena of metallic conduction are so complicated that they cannot be explained by one simple group of assumptions. So far we have considered only the heat conductivity due to the electrons. The atoms themselves undoubtedly transfer a part of the heat motion as is shown by the fact that non-conductors of electricity have finite values of λ while σ is equal to zero. Moreover, there are good reasons for believing l, the mean free path, is a function of the temperature. This would follow from Richard's theory in regard to the variation of the radius of the atom. It should be pointed out that if we take the two most simple formulas

$$\lambda = \frac{1}{3} Nlv\alpha,$$

$$\sigma = \frac{Nle^2}{2mv},$$

and assume $\frac{1}{2}mv^2 = \alpha T$ and also $l = \text{const} / \sqrt{T}$, it follows that λ becomes independent of the temperature, while σ is inversely proportional to the absolute temperature. This agrees fairly well with experimental facts over a considerable range of temperature. That the mean free path has something to do with the conductivity is also shown by the Hall effect. H. Kamerlingh Onnes has found that the constant of the Hall effect for gold, silver and mercury, increases considerably near the temperature of liquid hydrogen.

Finally, the electric field may act on the atoms in a metal, tending to bring about a certain polarization which will have an effect on the conductivity for electricity and heat. If this were the case, we should expect the use of temperature baths to lead to a value of λ different from that obtained by electric heating.

It was the purpose of the present investigation to attempt to bring further evidence in favor of one of the different theories. The alkali metals were thought to be particularly suited to this purpose because they have properties quite different from those of the other metals. Alkali metals have a higher temperature coefficient of resistance than the other metals. The atomic heat and atomic volume are greater and the index of refraction smaller than for the ordinary metals. In their photoelectric properties they differ considerably from the other elements. All these properties indicate that the alkali metals are rich in electrons and that even the positive "rest-atoms" have considerable mobility.

So far as known, the heat conductivity of the alkali metals has hitherto not been measured. This is a constant of sufficient importance to make its determination worth while. Northrup[1] has determined the electrical conductivity of the alkali metals by a very good method and claims an accuracy of one half of one per cent. His results, however, do not agree well with those of former observers[2] and it was therefore considered important to check his work by an entirely different method.

II. Theory of the Method.

The original Kohlrausch[3] method, which was perfected by Jaeger and

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[1] E. F. Northrup, Trans. Am. Electro-Chem. Soc., Vol. XX., 1911, p. 185.

[2] Mattheisen, Phil. Mag. (4), 12, 199, 1856; 13, 81, 1857. Bernini, Phys. Zeit., 5, 241, 1904.

[3] F. Kohlrausch, Gött. Nachr., S. 83, 1874; Pogg. Ann., 156, S. 616, 1875; Ann. der Phys., (4) I., 145, 1900.

Diesselhorst,[1] was used. It is both simple and reliable and it has the distinct advantage of giving the ratio of the heat and electrical conductivities directly. This method consists, briefly, in sending a steady electric current through a cylindrical rod of the metal to be investigated and measuring the temperature and potential difference at three equidistant points along the axis of the rod, while the temperatures of the ends of the rod and of the surrounding jacket are held constant. For the convenience of the reader the theory of the method, so far as it has any application to this investigation, will be given here in a simplified form.

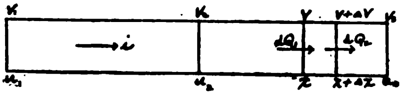

Fig. 1.

Referring to Fig. 1, let u and v represent the temperature and potential of any cross-section of the rod; and let

a = area of cross-section,

σ = electrical conductivity,

λ = thermal conductivity.

Let us assume that the Thomson effect is negligible and that λ and σ, for the small temperature interval considered, are constant. Then the current flowing through the rod is given by

$$i = \left(-\frac{dv}{dx}\right)\sigma a.$$

And the number of calories of heat developed in the elementary volume per unit time is

$$dQ = \frac{i^2}{\sigma}\cdot\frac{dx}{a}\cdot\frac{1}{J},$$

where J represents Joule's equivalent,

$$dQ = \left(\frac{dv}{dx}\right)^2 \sigma a \frac{dx}{J}.$$

The quantity of heat flowing into the elementary volume per unit time is

$$dQ_1 = \left(-\frac{du}{dx}\right)\lambda a,$$

and the quantity flowing out is, likewise, equal to

$$dQ_2 = -\frac{du}{dx}\lambda a - \frac{d^2u}{dx^2}\lambda a dx.$$

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[1] Jaeger und Diesselhorst, Wiss. Abh. der Phys. Tech. Reich., 3, 269, 1890; Sitz. Ber. Der Berlin Ak. d.w., 38, 719, 1899.

For the stationary state

$$dQ + dQ_1 - dQ_2 = 0. \qquad (1)$$

Substituting in this equation, we have

$$\left(\frac{dv}{dx}\right)^2 \frac{\sigma}{J} + \frac{d^2u}{dx^2}\lambda = 0. \qquad (2)$$

Now the isothermal surfaces are also equipotential surfaces, if we assume that the temperature is constant for all points of the same cross-section, and the temperature depends upon the potential only. Then

$$\frac{du}{dx} = \frac{du}{dv}\frac{dv}{dx}.$$

And

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2 + \frac{du}{dv}\frac{d^2v}{dx^2}.$$

But

$$\frac{d^2v}{dx^2} = 0,$$

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2.$$

Substituting this value in equation (2), we have

$$\left(\frac{dv}{dx}\right)^2 \frac{\sigma}{J} + \lambda\frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2 = 0.$$

Or

$$\frac{d^2u}{dv^2} = -\frac{\sigma}{J\lambda}. \qquad (3)$$

Integrating this equation, we have

$$\frac{\lambda J}{\sigma}u = -\frac{v^2}{2} + Av + B. \qquad (4)$$

The integration constants, A and B, are readily evaluated by imposing the condition

$$u_1 = u_3 = u',$$

and the equation can be reduced to the form

$$\frac{\lambda}{\sigma} = \frac{1}{8}\cdot\frac{1}{J}\cdot\frac{(v_1 - v_3)^2}{u_2 - u'}, \qquad (5)$$

where u_2 is the temperature of the middle of the rod, and u' is the temperature of either of the two sections equally distant from the middle.

Equation (5) would be true if no heat were lost through the lateral surface of the rod. This condition, however, cannot be realized experimentally and so it is necessary to apply a correction.

Let us change (5) slightly by expressing λ in watt-seconds, instead of calories, and put

$$V = \tfrac{1}{2}(v_1 - v_3),$$

$$U = u_2 - u' = u_2 - \tfrac{1}{2}(u_1 + u_3).$$

Then we have

$$\frac{\lambda}{\sigma} = \frac{V^2}{2U}. \qquad (6)$$

In this equation, then, U stands for the value of the temperature difference, supposing that the surface of the rod were covered with a perfect heat insulator.

Now let Δ represent the observed value of the temperature interval $u_2 - \tfrac{1}{2}(u_1 + u_3)$; let u_0 represent the temperature of the surrounding jacket; and let

$$N = u_0 - u_2 + \tfrac{1}{6}\Delta.$$

Then, as Jaeger and Diesselhorst have shown,[1]

$$U = \Delta - \epsilon N, \qquad (7)$$

where ϵ is a correction factor depending on the conductivity of the packing, the conductivity of the metal, and the dimensions of the rod experimented upon; and its value can be determined by experiment.

In the present work with the alkali metals, the values of λ/σ were computed by means of equations (6) and (7).

$$\epsilon = \frac{\Delta}{N},$$

for the case where no heating current is used. The method of obtaining this correction factor will be made clear in a later chapter.

III. APPARATUS.

End Baths.—The apparatus for controlling temperatures was constructed in the department shop. It was modeled after that of Jaeger and Diesselhorst, but certain modifications were necessary in order to protect the glass vacuum tubes which contained the alkali metals. The end baths were provided each with a flat brass lid and a rotary stirrer, as shown in Fig. 2, which was driven by a small motor. Fig. 3 indicates the method used to attach the glass tubes to the end baths. In a way to be described in detail later, the metal to be studied was poured into glass tubes one or two centimeters in diameter and 30 cm. long. The ends of the tube were closed by copper discs, 2 mm. thick and 5½ cm. in diameter. By means of suitable brass rings, each provided with six screws, the end-discs were attached to annular diaphragms which, in turn, were mounted against the end baths in a similar way so that the alkali metal and the water were separated only by the thin discs of copper. The soft-rubber diaphragms served as a protection for the glass tubes against mechanical strains.

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[1] Wiss. Abh. der Phys. Tech. Reich., 3, 285, 1900.

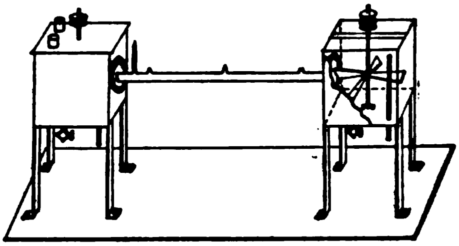
Fig. 2.

The heating-current terminals were introduced beneath the heads of three of the screws symmetrically placed with respect to the center of the discs.

Brass Jacket.—The temperature of the atmosphere of the tubes was controlled by pumping water from a reservoir through a cylindrical brass jacket by means of a small turbine. This jacket was made in two independent parts which were connected at *A* and *B* (Fig. 4), and similarly on the opposite side, by short rubber tubes, thus making it necessary for the water to flow the entire length of both semi-cylinders before leaving the jacket. The wires of the thermo-couples were introduced between the two parts of the jacket and were insulated from the brass by thin strips of mica.

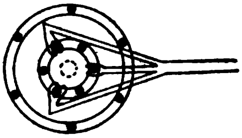
Fig. 3.

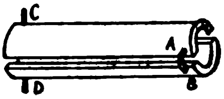

Fig. 4.

The temperature, u_0, of the jacket was measured by two Beckmann thermometers, mounted deep within vertical glass tubes through which the water flowed, so that no stem corrections were necessary. Moreover, these thermometers were placed so that their bulbs were at exactly equal distances from the points C and D respectively. The tubes leading from the jacket to the thermometers were made as short as possible and were packed each with the same number of layers of asbestos paper. Likewise, the glass tubes containing the thermometers were packed similarly so that, even though the two indicated temperatures which differed considerably when working far from room-temperature, still the arithmetic mean of the two readings gave the true mean temperature of the water in the jacket.

The space surrounding the tube within the brass jacket was packed tight with cotton wool and the outside surface of the jacket was wrapped with fourteen layers of heavy cotton flannel.

Galvanometer.—The galvanometer used was of the D'Arsonval type and designed especially for work with thermo-couples. It has a resistance of 230 ohms, a period of four seconds, and a sensibility of 210 megohms for a scale distance of 1 meter. By means of an unusually good lens, however, the image of a lamp filament was brought to a sharp focus on a scale 5½ meters distant from the mirror. At 5½ meters the sensibility was 8.6×10^{-10} amperes per millimeter deflection. The E.M.F. of the copper-constantan thermo-couples was about 40 microvolts per degree, giving deflection of 0.2 mm. per 1/1000 degree. Thus a change in temperature of one thousandth of a degree could be detected.

Ammeters and other Apparatus.—Except for the potassium tube, where the value of the heating current sometimes exceeded 150 amperes, a new Siemens and Halske ammeter was used. It was standardized by means of a Wolff potentiometer, Weston standard cell, and a standard 0.01 ohm resistance. For the data on potassium a Weston direct reading ammeter (0–200) was used. This was put in series with the new ammeter, mentioned above, and calibrated for the range over which it was used.

All of the standard thermometers except No. 17,481 were standardized at the Reichsanstalt. No. 17,481 was certified by the Bureau of Standards. These thermometers were graduated to tenths of a degree.

An Otto Wolff potentiometer, Otto Wolff resistance boxes, and a Weston standard cell were used.

The heating current was supplied by the department storage battery.

Arrangement of the Electrical Apparatus.—The potentiometer, P, was connected as shown in Fig. 5. B_1 was a small storage cell; B_2, the standard cell; R_1, R_2 and R_3 were resistance boxes. By adjusting R_3 at the beginning of a run, the potential difference from A to C was made equal to the E.M.F. of the standard cell. R_1 and R_2 were kept constant.

The switches and keys of the potentiometer circuit which had to be operated continually while taking readings, were grouped together on one switchboard shown diagrammatically in Fig. 6. C_1 and C_2 represent commutators of the rocker type; S_1, S_2 and S_3 were two-way switches of the rocker type; K_2 and K_3 were ordinary mercury keys. Six blocks of paraffine were mounted upon a glass plate, 30 × 40 cm., in the positions indicated. The thirty-two mercury wells which were sunk in the paraffine, were all lined by small glass cups which served as supports for the metal rockers. These rockers were all made of copper and only copper wires dipped into the mercury cups, all being wound from the same spool. In this way, contact potential differences were reduced to a minimum.

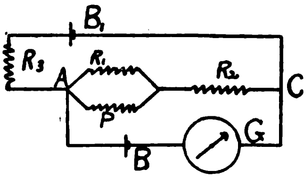

Fig. 5.

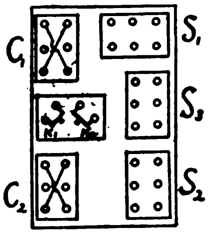

Fig. 6.

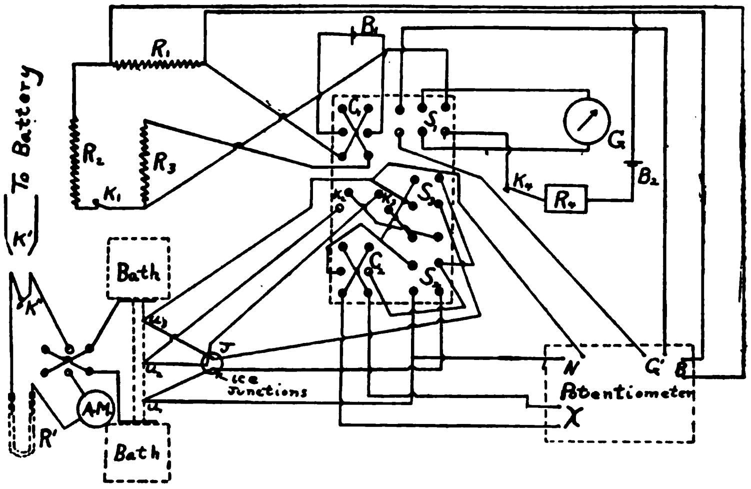

Fig. 7.

Fig. 7 shows a diagram of the exact connections of the electric circuits and the relative positions of the apparatus, with the exception of the galvanometer which was on a wall bench on the opposite side of the room, 5½ meters away. The ammeter, A.M., commutator C', controlling resistance R', and key K'', were all within easy reach of the observer. K'' was a short-circuiting key to avoid arcing when the rocker of C' was thrown over. R_4 was simply a protective resistance for the galvanometer and standard cell, and could be cut out of the circuit by a suitable plug.

IV. EXPERIMENTAL DETAILS.

Construction of Thermo-couples.—Since the alkali metals dissolve ordinary solder, it could not be used for the junctions which were placed in the tubes. Moreover, it was not an easy matter to hard-solder the junctions without burning the minute copper wires. Several attempts to do this having failed, it was decided to try the use of mechanical contacts. The fine copper wire, 0.12 mm. in diameter, was wound around the constantan wire (diam. 0.18 mm.) for a distance of about 2 mm. The shape of these junctions was admirably adapted to the double purpose of measuring both the temperature and potential difference between two cross-sections. They were mounted in a tube of sodium-potassium alloy but the data was inconsistent and on removing the junctions from the tube and attempting to check their calibration, it was found that two of the three calibration curves had shifted by an amount equivalent to more than one tenth of a degree.

So it was considered necessary to solder the wires together. The method which finally succeeded was as follows. Nearly equal weights of copper and silver were melted together with a small blast flame. A junction formed by two or three turns of the copper wire around the constantan, was moistened and covered with powdered borax. Then, at a time when the temperature of the silver-copper alloy was just above the melting point, the junction was dipped beneath the surface of the globule and quickly removed.

Junctions could be soldered in this way without any injury to the delicate wires. Such junctions, therefore, were used in the last three tubes experimented upon,—the three for which the data are given in this paper. The ice junctions were soldered with ordinary soft-solder.

For the alloy tube and the potassium tube, copper wire 0.12 mm. in diameter was used. However, it was found to be almost impossible to go through the long process of calibrating the thermo-couples, mounting them into the tube, filling the tube, and finally mounting the tube between the water-baths, without breaking one of these frail wires at some point where it could not be soldered,—thus involving the loss of the thermo-couple and several days' work. Consequently, somewhat larger copper wires were used in the sodium tube. In this case the diameter of the wire was 0.16 mm. It can be shown, however, that the error due to the conductivity of this wire was negligible for the conditions under which it was used. For all three of the tubes the constantan wire used had a diameter of 0.18 mm.

Platinum-constantan thermo-couples were used in the lead rod because, at that time, it was thought platinum wire would be used in the case of the alkali metals since it could be sealed into the glass, but the plan proved impracticable.

Calibration of the Thermo-couples.—The thermo-junctions and thermometer were mounted within a large Dewar flask which contained also a rotary stirrer. For the lower temperatures salt and ice were used to keep the temperature from rising, while for the higher temperatures steam was introduced slowly through a small tube near the wall of the flask at a point diametrically opposite the position of the thermo-junctions and thermometer. The temperature in this way could be held very steady by regulating the gas pressure of the three Bunsen flames which heated the boiler. The rotary stirrer was run by a small motor.

For the first few calibration curves a cathetometer was used to read the thermometer scale. This, of course, was a most accurate method, but it involved the difficulty of holding the temperatures constant for several minutes at a time, since the vernier had to be adjusted and read both before and after balancing the potentiometer for direct and reversed currents. Consequently, it was decided to try a direct-reading eye-piece attached to the stem of the thermometer. By this method the data for a point on the calibration curve could be obtained so much more quickly that the loss in accuracy of the scale reading was almost compensated by the gain in time and consequent smaller variation in the temperature. Readings were taken at intervals of about one or two tenths of a degree over the particular range where the curves were to be used and, when the points were plotted, there was no doubt about the proper position of the line.

The curves obtained in this way were reliable to about three or four thousandths of a degree, for the measurement of temperature differences; and, since this was as high a degree of accuracy as was required in the calibration, the use of the cathetometer was abandoned in favor of the quicker and less laborious procedure.

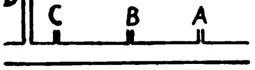

Fig. 8.

Preparation of the Tubes.—The kind of tube used to contain the alkali metals is shown in Fig. 8. The side tubes A, B and C, through which the thermo-junctions were introduced, were about 2 mm. in diameter and 10 cm. apart. They were sealed on in such a way as to change the cross section of the main tube as little as possible. The filling tube *D* was always placed at least 4 cm. from *C*. The diameters of the tubes are given in the data tables. The entire length in each case was about 30 cm.

Considerable difficulty was met in devising a method of sealing in the thermo-junctions so that a vacuum could be maintained at temperatures above the melting point of sealing wax. It was finally accomplished in the following way. The two wires of the junctions, one of which in each case was contained in a minute, slightly funnel-shaped glass tube for insulation purposes, were first sealed into the tube by means of "Quixo Caementium." This is a mineral cement, a commercial article, which was purchased from one of the local dealers. It dries very hard but it is somewhat porous and will hold a vacuum only a short time. Consequently, after the caementium had dried it was covered over with a layer of sealing wax. A kind called De Khotinsky cement was used because it has a higher melting point than the red, "Bank of England" wax. The caementium held the thermo-junctions rigidly in their positions and when the tube was heated the air pressure could not force the soft wax into the tube.

After grinding the ends of the tube they were fitted into circular grooves in the copper end-disks, about 1.5 mm. deep. These joints were filled with litharge (PbO) mixed in boiled linseed oil, and baked for several hours at a temperature of about 100° C. When thoroughly dry and solid they were covered with a thick layer of the Khotinsky sealing wax. The reason for using litharge in place of caementium, for sealing on the end discs, was the fact that it does not dissolve in water,—thus reducing the fire-risk in case of accident.

Before the end discs were sealed on, an accurate scale was introduced within the tube and the thermo-junctions bent into positions which spaced them exactly 10 cm. apart. They extended about 3 mm. into the tube.

The sodium and potassium tubes were prepared as described above. Sealing wax alone, however, was used in the case of the sodium-potassium alloy and for this reason no data could be taken with this tube for temperatures above 45°.

Filling the Tubes.—The method of filling the tubes is illustrated in Fig. 9. The sodium or potassium was introduced into the bulb *D* through an opening at *G*. The tube was then sealed at *G* and the Gaede pump started. After melting the metal, it was kept hot for an hour or more during the exhaustion, in order to drive off all traces of the oil. When the crust finally appeared dry and black, and the discharge tube *F* showed only the presence of the alkali vapor, the system was sealed off at *E*.

Then, holding *AB* in a horizontal position and keeping it hot with Bunsen flames, the tube *D* was tilted and the bright, pure metal poured through a system of small funnels at *C* which held back all of the dross.

It was a very difficult matter to fill a tube because of the formation of bubbles due to vapor pressure, and further, because of the contraction of the metal on cooling. The only way it could be done at all was to pour in metal a little at a time and allow it to solidify before adding any more. Thus it was necessary to melt the successive portions together to avoid layers and this local heating often involved the loss of a tube, either by breaking the glass or by letting the air in through the softened cement at one of the thermo-junctions. When filled, the tube *AB* was sealed off at a stricture *H* and it was then ready to be mounted between the water-baths.

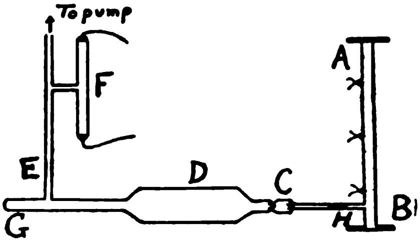

Fig. 9.

Purity of the Metals.—The sodium and potassium were purchased from Eimer and Amend and, in a personal letter from the company, were claimed to be "very pure." I am indebted to Dr. G. McP. Smith, of the chemistry department, for the following test on the purity of these metals.

Sodium.

1. Free from iron (KCNS test).
2. Free from calcium ($(NH_4)_2C_2O_4$ test).
3. Free from magnesium (Na_2HPO_4 test).
4. Free from aluminum (no ppt. with $NH_4OH-Na_2HPO_4$ test).
5. Free from potassium (H_2PtCl_6 test).

Spectroscopic test also negative, but conditions were not most favorable at time of test.

Potassium.

1. Free from iron.
2. Free from calcium.
3. Free from magnesium.
4. Free from aluminum.
5. Contains enough sodium to give a test with the spectroscope. Undoubtedly only a trace.

Method of Control of Temperatures.—The apparatus for controlling temperatures has been described in Chapter III. For the determinations above room temperature, the temperatures were adjusted and held constant by means of Bunsen flames, one under each end-bath and three beneath the large reservoir from which the water was pumped through the brass jacket. For the lower temperatures the turbine was discarded and cold water was run through the jacket by gravity pressure, the rate of flow being regulated by a small globe valve. In these determinations the temperatures of the end baths were watched constantly by a student helper and were maintained by the continuous addition of snow and salt.

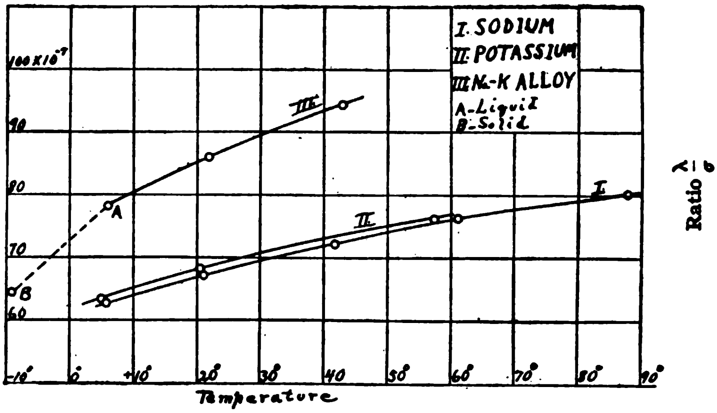

Fig. 10.

Regulation of the Heating Current.—As already mentioned, the currents from the large storage battery were remarkably constant. The slight regulation necessary was accomplished with a mercury rheostat. The U-tube, which was made of glass tubing 2.6 cm. in diameter, stood 80 cm. high. Continuous adjustments could be made by varying the position of the copper-plated iron rods which dipped into the mercury.

V. DATA TABLES AND CURVES.

In order to cut down the length of the paper the original data will be given only for a few typical runs. They will serve to illustrate the method

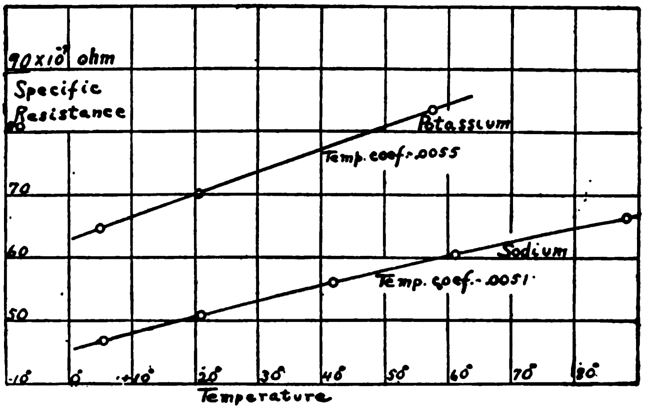

Fig. 11.

of taking observations and to indicate the degree of consistency obtained at different temperatures. In the tables which follow these "specimen runs," merely the final results are recorded.

Meaning of Symbols.—In all the data tables the following notation is used:

r_1, r_3 = balance-resistance on potentiometer dial for thermo-couples No. 1 and No. 3.

r_2 = balance-resistance for thermo-couple No. 2 at middle of tube (or rod).

r' = balance-resistance when reading P.D.

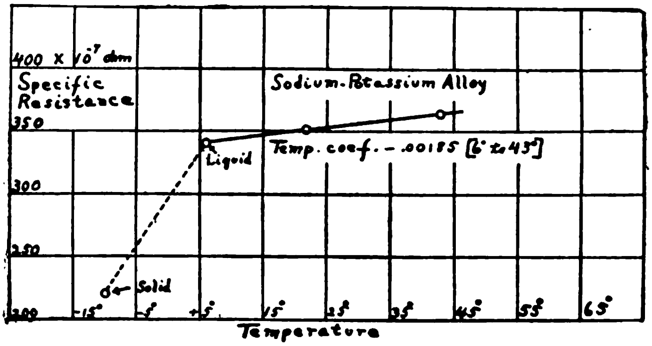

Fig. 12.

u_1, u_2, u_3 = temperatures corresponding to resistances r_1, r_2, r_3.

u_0 = temperature of the brass jacket.

$u' = \frac{1}{2}(u_1 + u_3)$.

$t_m = \frac{1}{2}(u' + u_2)$ = temperature for which the values of σ/λ, ρ and λ are taken in plotting curves.

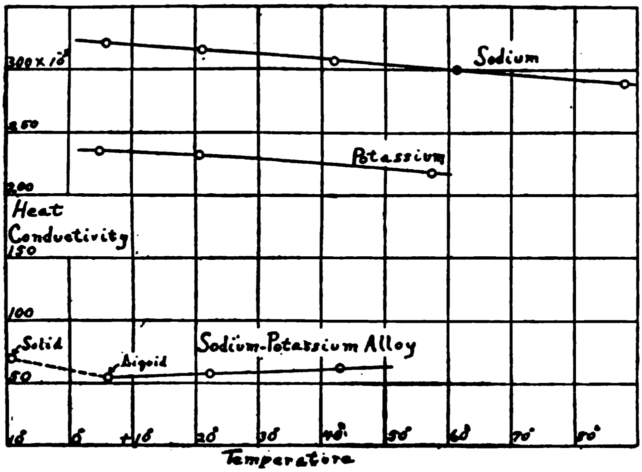

Fig. 13.

V = one half of the P.D. between the two points which were held at the same temperature.

I = value of heating current in amperes.

$\Delta = u_2 - u'$. $U = \Delta - \epsilon N$.

$N = u_0 - u_2 + \frac{1}{6}\Delta$. $\epsilon = \Delta/N$ when $I = 0$.

The letters D and R in the tables represent direct and reversed currents through the potentiometer to eliminate contact potential differences.

No. 2606 and No. 2607 refer to the two Beckmann thermometers which gave the temperature of the brass jacket.

Table I.

Constants for the Three Tubes.

Substance.	Inside Diameter.	Area a.	Effective Length l.
Na-K Alloy	1.562 cm.	1.916	20 cm.
Potassium	1.620 cm.	2.061	20 cm.
Sodium	1.234 cm.	1.196	20 cm.

$$\rho = \frac{Ra}{l} = .0958R = \frac{.0958 \times 2V}{I}, \text{ for sodium-potassium alloy.}$$

$$\rho = \frac{0.103 \times 2V}{I}, \text{ for potassium tube.}$$

$$\rho = \frac{.0598 \times 2V}{I}, \text{ for sodium tube.}$$

Table II.

Correction Factor for Potassium Tube (Specimen Run).

	r_1	r_3	r_2	u_0 No. 211.	u_0 No. 212.
D	187.8	187.7	197.2	2.20	1.36
R	186.8	186.8	196.2		
D	187.5	187.8	197.0	2.18	1.35
R	186.6	186.9	196.2		
D	187.5	187.8	197.0	2.19	1.30
R	186.7	186.9	196.3		
D	187.5	187.6	196.9	2.20	1.27
R	186.7	186.7	196.2		
D	187.1	187.8	196.9	2.23	1.24
R	186.4	186.9	196.1		

Left bath held at 18.4°; right bath at 18.3°.

Mean temperature on No. 211 = 2.20 + 33.06 = 35.26°.

Mean temperature on No. 212 = 1.30 + 32.91 = 34.21°.

$u_0 = \frac{1}{2}(35.26 + 34.21) = 34.74°$ C.

Mean r_1 = 187.1 ohms; u_1 = 20.025°.

Mean r_3 = 187.3 ohms; u_3 = 19.965°.

Mean r_2 = 196.6 ohms; u_2 = 20.925°.

$\Delta = 20.925 - 19.955 = 0.930°$.

$N = 34.74 - 20.925 + 0.155 = 13.97°$.

$$\epsilon = \frac{\Delta}{N} = \frac{0.930}{13.97} = .066.$$

TABLE III.

Sodium-Potassium Alloy at 5.7° (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r'	r_1	r_2	r_3	u_0 No. 2606.	u_0 No. 2607.	r_1	r_2	r_3	r'
D	3667	33.9	35.9	68.4	4.05	4.30	34.9	35.7	68.8	3661
R		35.2	37.3	69.8	4.10	4.25	36.2	37.2	70.2	
D	3656	34.2	35.9	68.5	3.95	4.15	34.9	35.6	68.4	3664
R		36.0	37.3	69.9	3.95	4.20	36.7	37.2	70.3	
D	3656	34.2	35.9	68.6	3.94	4.20	34.8	35.5	68.4	3661
R		36.0	37.4	70.0	3.90	4.15	36.8	37.2	70.4	
D	3657	34.2	35.9	68.4	3.95	4.15	34.6	35.4	68.2	3663
R		36.1	37.6	70.2	3.93	4.15	36.6	37.2	70.2	
D	3658	34.1	35.7	68.3	3.98	4.17	34.6	35.4	68.1	3662
R		35.9	37.6	70.1	3.93	4.15	36.6	37.2	70.1	

Left bath at − 0.4°; right bath at 0°.

6 volts, 6 sets in parallel. $I = 41.2$ amp.

Mean $r_1 = 35.4$ ohms; $u_1 = 4.02°$. Mean reading on No. 2606 = 3.97.

Mean $r_2 = 36.6$ ohms; $u_2 = 4.04°$. Mean reading on No. 2607 = 4.20.

Mean $r_3 = 69.3$ ohms; $u_3 = 7.42°$.

$$\left.\begin{array}{l}\text{Mean temp. on No. 2606} = 3.97 + 2.41 = 6.38° \text{ C.}\\ \text{Mean temp. on No. 2607} = 4.20 + 2.76 = 6.96° \text{ C.}\end{array}\right\} u_0 = 6.67° \text{ C.}$$

Mean $r' = 3{,}660$ ohms. $2V = 3660 \times 4 \times 10^{-6} = .01464$ volt.

Sample Calculation.

$$\Delta = 7.42 - 4.03 = 3.39. \quad t_m = \tfrac{1}{2}(4.03 + 7.42) = 5.7°.$$

$$N = u_0 - u_3 + \tfrac{1}{6}\Delta = 6.67 - 7.42 + 0.57 = -0.18.$$

$$U = \Delta - eN = 3.39 + 0.22 \times 0.18 = 3.43.$$

$$\frac{\sigma}{\lambda} = \frac{2U}{V^2} = \frac{6.86}{(.00732)^2} = 128.1 \times 10^3.$$

$$\rho = \frac{.0958 \times .01464}{41.2} = 34040 \times 10^{-9} \text{ ohm}.$$

$$\lambda = \frac{10^6}{4.19 \times 128.1 \times 3404} = .0547 \text{ cal}.$$

TABLE IV.

Sodium at Room Temperature (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r_1	r_2	r_3	r'	u_0 No. 2606.	u_0 No. 2607.	r_1	r_2	r_3	r'
D	187.6	190.9	218.0	3096	5.40	5.48	187.6	188.9	217.1	3099
R	187.0	190.3	217.4				188.7	188.0	217.9	
D	188.3	190.5	218.0	3093	5.43	5.52	187.7	188.9	217.3	3098
R	187.3	189.6	217.2				189.5	187.9	218.2	
D	188.7	190.9	218.6	3093	5.48	5.56	188.2	189.0	217.6	3098
R	187.7	190.3	217.6				189.3	188.2	218.4	
D	188.2	190.9	218.5	3093	5.53	5.61	188.1	188.9	217.4	3098
R	187.4	190.2	217.5				189.4	188.1	218.2	

12 volts, 12 sets in parallel. $I = 146.3$ amp.

Left bath held at 14.8°; right bath held at 15.9°.

Mean $r_1 = 188.2$; $u_1 = 20.08°$. Temp. on No. 2606 $= 5.46 + 18.08 = 23.54$.
Mean $r_3 = 189.5$; $u_3 = 20.12°$. Temp. on No. 2607 $= 5.54 + 18.05 = 23.59$.
Mean $r_2 = 217.8$; $u_2 = 23.01$. $u_0 = 23.57°$ C.
Mean $r' = 3{,}096$ ohms. $2V = 3{,}096 \times 4 \times 10^{-6} = .01238$ volt.
$\Delta = 2.91$. $N = 1.05$. $U = 2.85°$. $t_m = 21.5°$.

TABLE V.

Potassium at 57.8° (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r'	r_1	r_3	r_2	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	3075	560.6	554.4	584.5	3.38	2.75	557.6	558.4	584.4	3070
R		559.0	556.2	582.6	3.37	2.76	556.0	559.8	583.0	
D	3071	556.0	553.5	582.8	3.38	2.76	555.7	557.9	583.6	3070
R		557.8	555.2	581.0	3.42	2.77	553.8	559.6	582.0	
D	3078	557.4	554.9	584.1	3.43	2.78	557.7	557.6	584.3	3069
R		558.9	556.7	582.3	3.48	2.81	555.4	559.7	582.4	
D	3078	553.6	555.9	584.3	3.42	2.83	558.1	555.3	584.3	3079
R		555.3	560.6	582.5	3.35	2.81	555.6	557.1	582.4	
D	3074	554.4	555.9	584.4	3.27	2.73	557.8	555.2	584.0	3074
R		556.2	558.6	582.6	3.25	2.70	555.4	557.0	582.2	

16 volts, 8 sets in parallel. $I = 148.1 \times 1.026 = 152.0$ amp.
Left bath at 51.0°. Right bath at 51.3°.
Mean $r_1 = 556.6$; $u_1 = 56.625°$. Temp. on No. 2606 $= 3.38 + 54.98 = 58.36$.
Mean $r_3 = 557.4$; $u_3 = 56.630°$. Temp. on No. 2607 $= 2.77 + 55.13 = 57.90$.
Mean $r_2 = 583.2$; $u_2 = 59.070°$. $u_0 = 58.13°$.
Mean $r' = 3074$ ohms. $2V = .012296$ volt.
$\Delta = 2.443°$. $N = -0.53$. $U = 2.478°$. $t_m = 57.8°$.

TABLE VI.

Values of Correction Factor ϵ.

Substance.	u_0	u_2	Δ	N	ϵ
Lead rod	21.7	16. 7	0.918	5.38	0.171
Na-K alloy	21.19	15.40	1.35	6.01	0.224
	24.46	19.86	1.02	4.77	0.214
Potassium	34.74	20.925	0.930	13.970	0.066
Sodium	41.80	18.66	1.38	23.37	0.059

TABLE VII.

Complete Results for Lead (Commercially Pure).

Run No.	u_0	u_2	t_m	$2V$ $10^{-6}\times$	Δ	N	U	I Amp.	σ/λ $10^8\times$
1	21.64	21.94	20.6	1253	2.671	0.14	2.647	51.0	134.6
2	21.65	23.60	21.7	1566	3.838	−1.32	4.062	63.3	132.5
3	21.71	23.28	21.3	1588	4.046	−0.90	4.199	64.3	133.2

Remark.—For run No. 3, the lead rod was inside of a close-fitting glass tube.

Table VIII.

Complete Results for Sodium-Potassium Alloy.
(Masses taken proportional to the atomic weights.)

Run No.	u_0	u_2	t_m	$2V$ $10^{-6}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	−8.30	−8.28	−10.6	1511	4.56	+0.74	4.40	66.0	154.4	2193	.0705
2	−9.40	−6.37	− 8.9	1682	5.00	−2.20	5.48	72.9	155.2	2210	.0696
3	+6.67	7.42	5.8	1464	3.39	−0.18	3.43	41.2	128.1	3404	.0547
4	6.66	8.07	6.2	1588	3.83	−0.77	4.00	44.6	127.0	3411	.0551
5	22.40	23.936	22.0	1684	3.931	−0.88	4.122	45.9	116.3	3515	.0584
6	22.54	24.075	22.1	1702	4.003	−0.86	4.190	46.2	115.9	3527	.0584
7	22.66	22.395	20.7	1500	3.453	+0.84	3.271	40.9	116.2	3513	.0585
8	43.90	44.54	42.9	1550	3.17	−0.11	3.19	40.8	106.1	3640	.0619

Table IX.

Complete Results for Potassium.

Run No.	u_0	u_2	t_m	$2V$ $10^{-6}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	5.91	5.790	5.0	881	1.557	+0.38	1.531	141.9	158.2	649.2	0.232
2	6.58	5.810	5.0	862	1.525	+1.02	1.454	137.9	156.5	644.2	0.237
3	21.16	21.670	20.7	1035	1.965	−0.18	1.978	151.6	147.7	703.5	0.230
4	21.22	21.590	20.6	1030	1.920	−0.05	1.923	151.2	145.1	701.5	0.234
5	21.45	21.675	20.9	932	1.603	+0.04	1.600	137.6	147.4	698.0	0.232
6	58.13	59.070	57.8	1230	2.443	−0.53	2.478	152.0	131.1	833.8	0.218
7	57.91	58.510	57.4	1184	2.312	−0.21	2.326	147.3	132.4	835.3	0.216

Table X.

Complete Results for Sodium.

Run No.	u_0	u_2	t_m	$2V$ $10^{-6}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	7.20	6.97	5.7	1152	2.68	+0.68	2.64	147.7	159.0	466.4	0.321
2	7.75	7.22	5.8	1176	2.82	+1.00	2.76	150.7	159.5	466.7	0.321
3	23.42	22.12	20.9	1110	2.385	+1.70	2.283	130.6	148.2	508.3	0.317
4	23.57	23.01	21.5	1238	2.91	+1.05	2 85	146.3	148.8	506.0	0.317
5	43.32	43.44	42.1	1207	2.57	+0.31	2.55	128.3	139.7	562.6	0.304
6	44.97	43.38	41.7	1360	3.32	+2.14	3.19	145.5	138.1	559.0	0.309
7	62.30	62.84	61.3	1390	3.15	+0.01	3.15	137.2	130.4	605.8	0.302
8	63.11	62.83	61.4	1320	2.93	+0.77	2.88	130.7	132.1	604.0	0.299
9	89.01	89.43	88.1	1309	2.67	+0.03	2.67	118.0	124.8	663.4	0.288

VI. Discussion of Results.

In using the experimental method of obtaining the value of the correction factor ϵ for the alkali metals, it was necessary to assume that for the steady state the temperatures at corresponding points on the inside and outside surfaces of the glass tube were equal; *i. e.*, that the temperature gradient through the walls of the glass tube could be neglected in comparison with the drop in temperature through the cotton wool. One reason for making the runs with the lead rod was to find out if this assumption would introduce an error large enough to be detected Table VII. answers the question. The fact that the value of σ/λ for run No. 3 falls between those for runs No. 1 and No. 2, proves that the effect of surrounding the rod with the glass was smaller than other experimental errors. Lead was chosen for this experiment because of its low heat conductivity. The glass wall would have a still smaller effect in case of the sodium and potassium.

Another reason for taking the data for lead was to have a means of comparing my results with those of Jaeger and Diesselhorst. In this connection it should be noted that my average value of σ/λ for lead at 21.5° is 133.4×10^3 while that of Jaeger and Diesselhorst for pure lead, when reduced to 21.5°, is 138.2×10^3. This was considered a good check because the lead I used was only commercially pure. The presence of impurities always reduces the value of σ/λ.

As to accuracy of results it should be pointed out that for each run steady conditions were held for one to two hours and readings were taken continually during this time. Thus each value of u_1, u_2 and u_3, used in the calculations, depends upon sixteen to twenty readings on the potentiometer, while the values of V are computed from the mean of eight to ten readings. The current could be maintained much more nearly constant than could the temperatures and therefore the potential difference did not need to be read so often. Moreover, with one or two exceptions, every point on the curves represents the mean result of two or three independent runs.

The curves for λ/σ bend more than was expected. It would be interesting to know whether they become straight lines at higher temperatures. Judging from the behavior of other metals, this should be expected. Moreover, when $\lambda/\sigma T$ is plotted against T, these curves slope downward slightly with increasing temperature while Lees's curves for most of the pure metals bend slightly upward at ordinary temperatures. Thus sodium and potassium, like nickel, are irregular in this respect. It should be noted that the heat conductivities of sodium and potassium decrease slightly with increasing temperature, while the heat conductivity of the alloy *increases* with the temperature. This is the law followed by most metals and their alloys. The temperature coefficients of sodium and potassium are extremely high.

The mean values of the specific resistance of sodium and potassium at room temperature and the temperature coefficients are given below for convenience of comparison.

spec. res. of Na at 21.7° C. = 5072×10^{-9} ohm/cm.^{3}.
spec. res. of K at 20.7° C. = 7010×10^{-9}
temp. coef. of Na = .00513, range 6° to 88°
temp. coef. of K = .00552, range 5° to 58°

Northrup's Results.

spec. res. of Na at 20° C. = 4873×10^{-9}
spec. res. of K at 20° C. = 7116×10^{-9}
temp. coef. of Na = .0053, range 20° to 80°
temp. coef. of K = .0058, range 20° to 50°

Matthiessen's Result.

spec. res. of Na at 21.7° C. = 4464×10^{-9}

Bernini's Results.

spec. res. of Na at 0.0° = 4739×10^{-9}
spec. res. of K at 0.0° = 6644×10^{-9}

Bernini's results, when reduced to room temperature, are found to be higher than mine and Northrup's, while Matthiessen's value is seen to be lower. It is thought that my results agree with Northrup's as closely as could be expected, considering the wide difference in method. Indeed his method is the more accurate one for electrical conductivity. Consequently, the results of this investigation may be said to confirm Northrup's work on the resistance of sodium and potassium. The slightly smaller values of the temperature coefficients suggest that the metals used in this work may not have been quite as pure as those Northrup used.

SUMMARY.

1. The electrical conductivities of sodium, potassium and sodium-potassium alloy have been measured and the results are in agreement with the values obtained by Northrup.

2. The heat conductivities of the alkali metals have been measured for the first time, as far as known.

3. The temperature coefficients of these conductivities have been determined.

4. The resistance-temperature coefficients of potassium and sodium are extremely high.

5. The values of the ratio σ/λ for the alkali metals are extremely high.

6. The alkali metals behave in no exceptional way as regards the absolute values of the thermal and electrical conductivities at ordinary temperatures.

7. As a check on the method, the ratio σ/λ was determined for lead at room temperature and the value agrees with the one obtained by Jaeger and Diesselhorst.

8. A modification of the electron theory of metallic conduction has

been suggested which accounts for the variation of the specific heat with the temperature, and also explains the curves which Lees obtained for the ratio $\lambda/\sigma T$ for the pure metals at low temperatures.

In conclusion, I wish to acknowledge my indebtedness to Professor A. P. Carman, who has followed this work with continued interest, placing at my disposal all the facilities necessary for the investigation; and to Professor Jakob Kunz, under whose direction the work was done, for many good suggestions and for invaluable assistance in filling the tubes. I also wish to thank Dr. G. McP. Smith, of the chemistry department, who analyzed the metals used in this investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
May, 1913.

Note.—Since this paper was written, I note in the April number of Science Abstracts, which has just come, that W. Wien has published an article on "Electric Conduction in Metals" based upon the "quanta hypothesis." His theory may be similar to the modification suggested in this paper. The article referred to is not accessible in our library.

J. W. H.

COMPARATIVE STUDIES OF MAGNETIC PHENOMENA. V.

Change in Electrical Resistance Due to the Orientation of Oblate Spheroids within the Conductor.[1]

By S. R. Williams.

Introductory.

The change in electrical conductivity of ferromagnetic metals when subjected to a magnetic field was first observed in iron and nickel by Lord Kelvin[2] in 1856. His results showed that in both metals the electrical resistance was increased in a direction parallel to the magnetic lines of force and decreased in a direction normal. The qualitative results obtained by Lord Kelvin were for the most part confirmed by Adams,[3] deLucchi,[4] Beetz,[5] Tomlinson[6] and Goldhammer.[7] Beetz, in working with iron wires, failed to find any change in resistance in transverse fields. Tomlinson carried out some very extensive studies on the physical properties of certain metals and among them the alteration of electrical conductivity due to magnetic fields. His results are summed up in the following: "The electrical resistance of annealed iron and annealed steel, very hard steel, nickel, cobalt, bismuth and zinc are all increased by longitudinal magnetization." For transverse magnetization experiments were carried out in which the wires were circularly magnetized and a decrease in resistance was found. Goldhammer, from considerations of the Hall effect, was led to believe that there must be a change in resistance in all substances and greatest in those showing the largest Hall effect, as for instance in Te, Bi, Sb, Ni, Fe and Co. He did find a change in resistance in all of these but in Ag, Au and brass the effect was not large enough to measure with certainty. At the time of Lord Kelvin's experiments many expressed the view that the change in resistance was due to the mechanical deformations of the substances used. Goldhammer raised objections to this viewpoint and to obviate any deformations of the conductor, used his metals in thin deposits on glass. Three diamagnetic and three ferromagnetic metals were investigated, viz., Bi, Te, Sb and Ni, Co and Fe respectively. These metal films deposited on glass had two points of contact diametrically opposite and the plate was so arranged that it could be rotated about an axis normal to the plane of the glass. In this way the same points of contact could be used, but the direction of the flow of the current could be varied with respect to that of the magnetic field imposed upon it. His results are thus summed up: "Es nimmt also bei allen Metallen der Widerstand in der Richtung der Kraft linien zu; in der dazu senkrechten Richtung nimmt er nur in diamagnetischen Metallen zu; in magnetischen nimmt er ab." The hypothesis that change in resistance was due to deformations of the conductor, it seems, Goldhammer has pretty thoroughly disproved. Nickel, for instance, shortens its length for all field strengths applied longitudinally. Its resistance, according to Ohm's law, should decrease but instead we find it increasing when subjected to a longitudinal magnetic field.

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[1] Presented at the Cleveland meeting of the Physical Society, Dec. 30.

[2] Math. and Phys. Papers, Vol. 2, p. 307.

[3] Phil. Mag. (5), p. 153, 1876.

[4] Beibl., 7, p. 314, 1883.

[5] Pogg. Annal., 128, p. 202, 1886.

[6] Phil. Trans., 1883, p. 1.

[7] Wied. Annal., Vol. 31, p. 360, 1887.

Tomlinson concluded his study by saying that "the increase of resistance which is produced by magnetization is probably not merely due to the rotation of the molecules of the magnetized substance as molecules, but to the electrical currents which, according to Ampere's hypothesis, are constantly circulating around the molecules."

In 1900 Sir J. J. Thomson[1] explained this phenomenon on the corpuscular theory of electric conduction in metals. According to his theory, "the electric currents in the metal are carried by negatively charged corpuscles moving with a definite velocity under an applied E.M.F. These corpuscles are supposed to act as a perfect gas; consequently they have a mean free path and a mean velocity and exert a definite pressure. If the corpuscles are moving under an electric force and then a transverse magnetic force should be applied, the particles will move in cycloids, and the resistance will be increased. Similarly in a longitudinal field the electrons will describe spirals in their motion and again the resistance will be increased. It is to be noted that Van Everdingen[2] arrived at opposite conclusions regarding the transverse field effect in a theoretical paper which appeared not long after Thomson's. At the suggestion of Professor Thomson, Patterson[3] carried out a series of observations on the effect of a magnetic field on the electrical conductivity when applied transversely to the conductor. His experiments were performed on non-magnetic material such as German silver, copper, cadmium, zinc, gold, platinum, tin and carbon. In all of these conductors Patterson found that the transverse field tended to increase the resistivity unless in some metals which showed so little change that it was difficult to say just what did occur. Some of these same metal wires were also tested for the effect of a magnetic field applied in the direction in which the resistance was measured and here an increase was also found. His results are confirmatory of Thomson's theory so far as non-magnetic substances are concerned and seem to be a fairly satisfactory explanation. The theory, however, does not fit the results already cited for magnetic materials. Either the theory is not the proper explanation or else in the case of ferromagnetic conductors we have other factors in addition, which play important rôles. The latter seems plausible, as will be shown later, and possibly Van Everdingen's work may be utilized to fit the case of ferromagnetic substances.

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[1] Rapports presentes au Congres International de Physique, 3, p. 138, Paris, 1900. Phil. Mag., p. 353, March, 1902.

[2] Communications from the Physical Laboratory of Leiden, No. 72.

[3] Phil. Mag., p. 643, June, 1902.

Auerbach[1] has pointed out that in the Hall effect we have an E.M.F. developed normal to the lines of flow when the conductor is placed in a magnetic field and which ought to produce an apparent change in resistance. This is comparatively large in the ferromagnetic metals and may be one of the factors causing the difference in behavior of ferro and non-magnetic metals when placed in a transverse magnetic field.

We thus have many and varied reasons for this change in resistance, some of which are contradictory, but many are doubtless present and combine to give us the effects found.

Recently, I pointed out[2] that the majority of magnetic phenomena could be explained by assuming that the elementary magnet was an oblate spheroid about which negative electrons were revolving and that the orientation of such an elementary magnetic unit produced or at least influenced the magnetic phenomena which we know. If a ferromagnetic substance is made up of these oblate spheroids for the nuclei of the elementary magnets and the magnetic field gives them a definite orientation, what will be the effect on the electrical conductivity when the lines of flow are parallel to the equatorial planes of the spheroids and what will be the effect when the lines of flow are normal? In the thought that it might throw some light on this effect first discovered by Lord Kelvin, Mr. Paul Weeks, an advanced student in our department, has carried out the following experiments:

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[1] Winkelmann's Handbuch der Physik, p. 458, Vol. 5, Pt. 2, 1908.

[2] Phys. Rev., abstract, Feb., 1911.

Mr. Weeks' Experiments.

Wooden oblate spheroids, boiled in paraffine, were mounted, four on a wire, so that the equatorial planes contained the wires. The major axes were 1.74 cm. in length and the minor axes 0.82 cm. Sixteen such sets were completed and mounted so that the spheroids could be turned with the wires as axes. There were 64 spheroids and were grouped to form a cube as shown in Figs. 1 and 2. Fig. 1 is a vertical cross-section and Fig. 2 is a horizontal cross-section. These 64 spheroids were placed between two copper electrodes, 17 × 17 cm. square, and the whole inclosed in a paraffined wooden box with glass sides, as shown in Figs. 1 and 2. The box was 18 cm. deep and the horizontal cross-section, 17 × 17 cm.

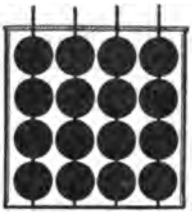

Fig. 1.

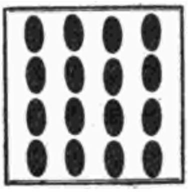

Fig. 2.

Ordinary tap-water was poured into the box until the spheroids and electrodes were covered. The resistance was then measured by means of a Kohlrausch bridge when the spheroids were all turned with equatorial planes normal to the lines of flow, when parallel and for intermediate azimuths between 0° and 90°. The difference was very marked, the resistance being much greater when the equatorial planes were normal than when parallel to the direction of the current. In Fig. 3 is shown the way in which the resistance varied as the angle between the equatorial

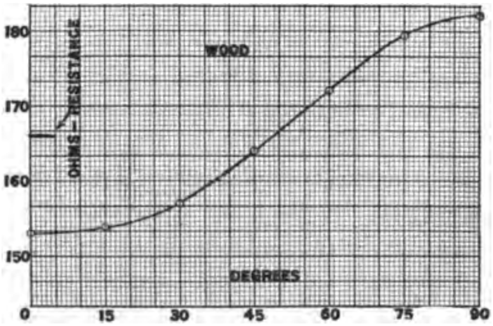

Fig. 3.

planes and the current were varied from 0° to 90°. A similar experiment was also tried with the same sized spheroids made of type-metal in which the spheroids themselves were better conductors than the tap-water. Similar results were obtained here as in the case of the non-conducting spheroids, viz., an increased resistance when the spheroids were set with equatorial planes normal to the current. For the metal spheroids the total resistance was less than for the wooden ones. The results are shown in Fig. 4. Acidifying the tap-water with H_2SO_4, and increasing the conductivity flattened the curves for the metal spheroids. If the tap-water had the same conductivity as the spheroids, orientation of the spheroids ought not to change the resistance.

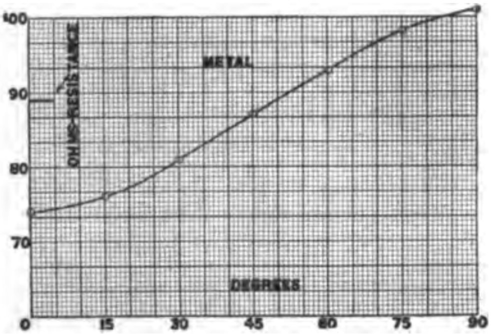

Fig. 4.

DISCUSSION OF RESULTS.

In the curves of Figs. 3 and 4 it is of interest to note that they are the same type of curve which one obtains when plotting the lengths of the diameter of the spheroid about an axis lying in the equatorial plane as the diameter swings through 90° or the same type of curve which one obtains in plotting the area of the projection of the spheroid on a plane as the spheroid is turned through 90°. To put it another way, if one used as radii-vectors the values of the resistances obtained when the spheroids were turned in the different azimuths, from 0° to 360°, the curve traced out by the termini of the radii-vectors would be an ellipse. Goldhammer[1] plotted his results in this way for the different values of the resistance of a conductor when placed in a magnetic field and also found that an ellipse was the figure obtained when a line was drawn through the termini of the radii-vectors representing the resistances for the different angles between the direction of the magnetic field and the lines of flow of the current.

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[1] *L. c.*

In a previous work[1] I have shown that to account for the changes in length of a ferromagnetic substance, when magnetized longitudinally, the orientation of oblate spheroids within the material would give the effects observed and that a shortening indicated that the obla te spheroids had their equatorial planes normal to the magnetic field. In iron and nickel this occurs in strong fields. Kelvin, Goldhammer, Tomlinson and Patterson worked with strong magnetic fields so that the oblate spheroids, if they exist, were oriented with their equatorial planes normal to the field. If resistance was measured normal to the field, then the current would flow parallel to the equatorial planes of the spheroids. For ferromagnetic substances this condition is the one for the decrease in resistance. It is also the condition found in the experiments reported here. Similarly, if the resistance is measured parallel to the field, there is an increase of resistance because the current flows normal to the equatorial planes. These experiments show increase in resistance when the current flowed normal to the equatorial planes. Thus for the metals which the theory of Thomson's did not cover, there is in these experiments a possible explanation. Cobalt lengthens for strong fields in which case it may be supposed that other factors, already mentioned, prevail. As was said above there can be little question but what we have a number of different factors combining to give us the effect described as change in resistance due to a magnetic field. It is a complicated phenomenon. In one metal one factor may predominate and in another some other factor may hold sway. In connection with the explanation offered in these experiments, it would be of great interest to measure the change in resistance of the Heusler alloys due to a magnetic field. They show increase in length for the Joule effect for all magnetic field strengths that have been studied.

The effect first found by Lord Kelvin is a comparatively small effect, hence strong magnetic fields are always used in studying it. If, however, the orientation of elementary magnets does play some part in this phenomenon, then we might expect a reverse effect for weak fields since the Joule effect shows a lengthening for weak fields and a shortening for strong in the case of iron and steel. The effect is doubtless too small to be detected in weak fields but nevertheless is worth trying for. This will be investigated in connection with a study of the Heusler alloys for change in resistance due to a magnetic field.

One point perhaps should be discussed: what is the cause of this change in resistance due to the orientation of the oblate spheroids within the conductor? If one maps the lines of flow about the spheroids, when the equatorial planes are normal to the lines of flow and when they are parallel, it will be seen that the length of the path of flow is greater when the equatorial planes are normal to the direction of flow than when parallel. This amounts to increasing the length of the conductor and so augmenting the resistance, although the distance between the electrodes remains constant. This is shown in Figs. 5, 6, 7 and 8 where 5 and 6 are for the non-conducting oblate spheroids and 7 and 8 are for the conducting spheroids. The lines of flow were plotted by a method described by Hering.[1] In Figs. 5 and 6 the elliptical openings are cut in the conducting sheet and so are non-conducting, while in Figs. 7 and 8 zinc ellipses are laid on the conducting sheet and are better conductors than the sheet itself. There will also be a change in resistance due to change in cross-section of the electrolyte as the spheroids are rotated. This is also shown in Figs. 5, 6, 7 and 8.

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[1] PHYS. REV., Vol. 34, p. 40, Jan., 1912.

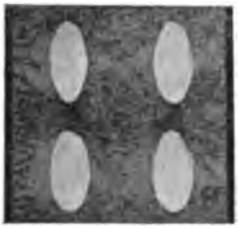

Fig. 5.

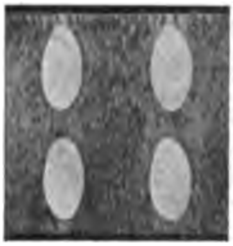

Fig. 6.

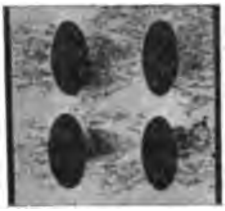

Fig. 7.

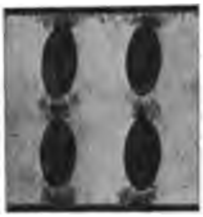

Fig. 8.

The experiments as carried out were with the condition that the distance between centers of the spheroids remained constant. This is analogous to Goldhammer's experiments in which he used thin films plated on glass. The elementary magnets could not shift laterally. The resistance was also measured when the distance between the bounding surfaces was the same in both directions, the distance between the electrodes remaining as before. This did not seem to affect the general results, observed when the centers were kept fixed. The heavy, horizontal lines in Figs. 3 and 4, marked by an arrow, indicate the resistance when the spheroids are turned in all possible directions. This would be analogous to the condition of a ferromagnetic substance in the virgin state.

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[1] Hering's Essentials of Physics, p. 298.

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THE PHYSICAL REVIEW.

ROTATIONS IN THE IRON ARC.

By W. G. Cady.

§ 1. Reference has been made in previous papers[1] to a peculiar type of rotations found at the anode of the iron arc in air. Subsequent experiments have shown that the phenomenon is more complicated than was at first supposed. Stated briefly, if the anode is sufficiently oxidized so that a smooth molten globule of oxid is formed, the positive base of the arc tends to fall into a circular motion, producing the appearance of a minute ring of light at the anode. As the current is increased from about 1.5 to 2.5 amperes, four characteristic types of rotation may be observed in succession, the transition from one type to the next being marked by a distinct and sudden change in diameter and frequency of rotation. This is not the result of artificial conditions, but the *normal sequence of events* in the iron arc as the current increases.

Apparatus and Method.

§ 2. Since we are dealing with an effect that depends essentially upon the anode, any substance that does not, by distilling across the arc, change the chemical nature of the anode, may serve as cathode. An iron cathode serves fairly well, but the wandering of the negative base is troublesome. I have secured the best results by using as cathode a cored carbon half an inch in diameter. Apparently the traces of salt in the carbon tend to hold the negative base steadier at the small currents with which we have here to do. Care must however be taken not to let the arc take place directly from the core, as the metallic salts from the core change the form of the discharge to a glow at the anode, so that the first stage[2] persists even for currents over five amperes. It was found best to remove the core, leaving a bore through the center of the carbon. The negative base of the arc occupied only a small spot on the side or end of the carbon. No advantage was found from impregnating solid carbons with various salts. The anode may be either above or below, in the form of an iron rod from 3 to 6 mm. in diameter with oxidized end, or a small bead of oxid resting in a depression on the end of a carbon holder. The length of arc in the present experiments varied between 3 and 10 mm.

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[1] Am. Jour. Sci., 24, p. 405, 1907; Phys. Rev., 24, p. 381, 1907, and 35, p. 77, 1912; Phys. Zeitschr., 8, p. 890, 1907.

[2] Cady and Arnold, Am. Jour. Sci., 24, p. 384, 1907.

Most of the experiments recorded here were performed with the brass water-cooled lamp shown in Fig. 1. As this apparatus has been found useful in various lines of work, the following brief description is given. It consists of an inner vertical cylinder *TT* of brass 18 × 9 cm., with flat top and bottom, completely inclosed in an outer brass jacket. Water is kept flowing in at *A* and out at *B*. *C* and *D* are brass tubes for inlet or outlet of gases. *E* is a round horizontal brass disk on the end of a vertical brass stem with hard rubber handle *G*, which can be rotated about a vertical axis by means of a ground glass joint. The stem is sealed into the lower member of the joint at *M*. The upper member of the joint, *N*, is sealed into a brass tube, which is soldered to the inner and outer jackets. The joint is thus kept cool. The disk *E* carries six brass sockets (two of which are shown), in which various electrodes may be fastened. A convenient interchange of electrodes is thus made possible without opening the lamp. For the present purpose this was an important consideration, since the rapid and irregúlar wearing away of the carbon cathodes made frequent changes necessary. *F* is the upper electrode, controlled by a rack and pinion movement. The stem for turning the pinion passes through a horizontal glass joint (not shown) similar to that at *E*. In front is a round opening passing through the inner and outer cylinders, indicated by a dotted line in Fig. 1. A glass window can be screwed tightly over this.

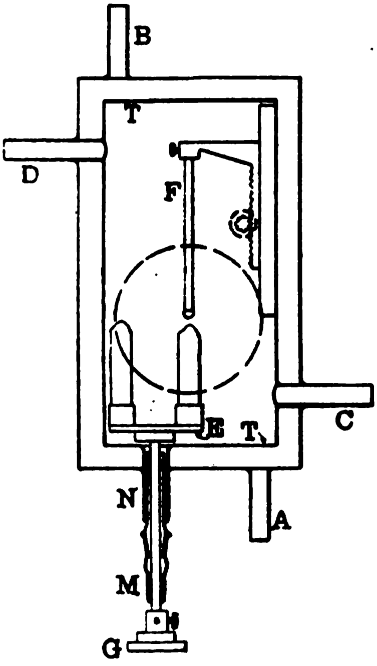

Fig. 1.

For the experiments in free air the window was generally left open. But since the rings are best observed when disturbing air-currents are eliminated, it was sometimes necessary to close the opening and to draw a slow current of air through the lamp, in order to maintain the supply of oxygen.

In order to make the rings visible from the front, the cathode was generally brought into such a position as to cause the arc to take place from a point on the front of the anode globule.

§ 3. The following methods were employed, singly or together, in studying the appearance of the anode and the accompanying oscillations.

1. A large image of the arc was projected on to a screen.
2. The frequency of the oscillations could be approximately determined by comparing with a tuning fork the high-pitched whistle that accompanied the rotations.
3. To detect small periodic effects, especially when there were disturbing noises, a high-resistance telephone receiver, shunted by about one ohm, was connected in series with the arc. The receiver responded to the small fluctuations in current which, as will be seen, always accompany the rotations.
4. By reflecting the image from a rotating mirror, the movements of the positive base could be roughly examined. Although no stationary image could be obtained in this way, still valuable knowledge of the character of the movements was gained.
5. The fluctuations in current and potential drop were recorded with a Duddell high-frequency oscillograph and rapidly moving film.
6. A somewhat enlarged image of the arc was in some cases photographed on the moving film, alone or simultaneously with the oscillograph records.

All the characteristic phenomena can be observed with a supply of 110 volts, but in general from 150 to 300 volts were used, as the arc was then more stable. A liquid resistance was used for fine regulation of current.

Description of the Rotations.

§ 4. *Type A.*—Up to about 1.5 amp. the anode globule, though brightly incandescent, is not vaporizing, *i. e.*, the arc is on the first stage with a glow discharge at the anode. At about 1.5 amp. the change to the second stage generally occurs, when the current increases abruptly one or two tenths of an ampere. The positive base of the discharge then concentrates itself upon a spot similar to that at the cathode, and a hissing sound is heard, due to the vaporization. A close examination of the magnified image, however, reveals the fact that the positive base is in the form of a ring with dark center, about 0.4 mm. in diameter, while under favorable circumstances a faint wavering high-pitched note can be heard.

This is the first of the four types of rotation referred to above. For brevity we will call it "Type A," or "Ring A." The measured frequency *f* and diameter *δ* of this as well as of the other three types are shown in Fig. 2. The data for this figure are mostly taken from a single photographic film. The drum carrying the film was kept turning at the rate of 10 rev. per sec. during the operation. The "life history" of all four types was recorded as a practically continuous record about eleven feet long on this film. This was done by gradually decreasing the resistance in the arc circuit, while simultaneously the lens that projected the image of the positive base on to the film was moved sidewise by hand at as uniform a rate as possible. The values here shown were confirmed by other observations, photographic and visual, and may be taken as representative of the normal phenomena, except that the changes on this film took place at somewhat smaller currents than is commonly the case. In single instances, more or less wide departures from these values must be expected, for while the *relative* values of *f* and *δ* in any experiment are generally in agreement with Fig. 2, still the *absolute* values may differ very widely. Hence averages from different tests are sometimes untrustworthy.

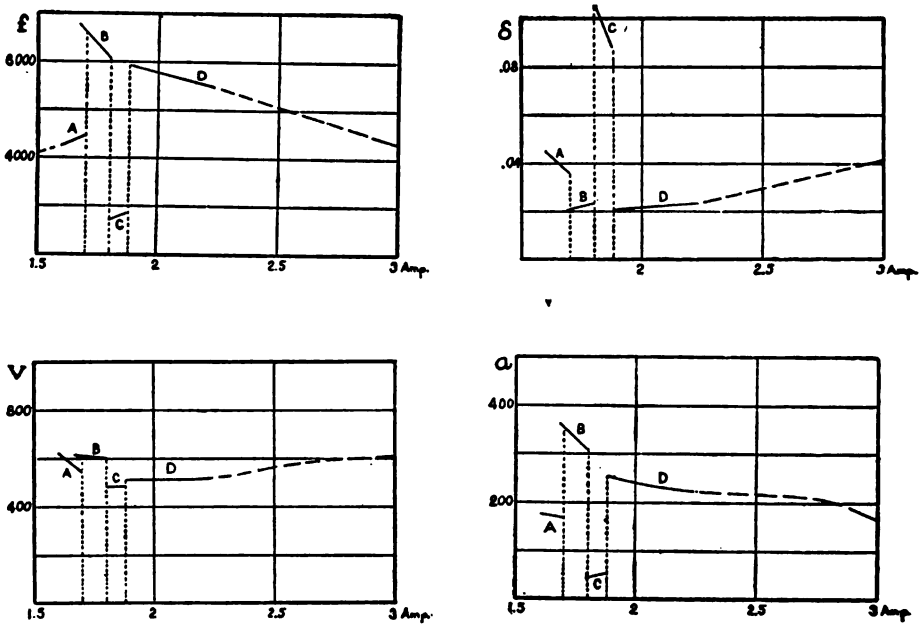

Fig. 2.

Dependence of frequency *f* (cycles per sec.), diameter of ring *δ* (cm.), linear velocity *v* (cm. per sec.), and normal acceleration *a*, upon the current, for the four types of rotation.

The broken lines in Fig. 2 are based on other data gathered at different times.

§ 5. *Type B.*—Between 1.67 and 1.73 amperes the second type of rotations, which we will call Type B, begins to assert itself. This ring, as seen in Fig. 2, has a smaller diameter and higher frequency than Type A. It appears on the film first in short trains interjected at intervals in the midst of Type A. This is seen in the first curve in Fig. 3. The long waves are Type A, the short ones Type B; for each type, the frequency is higher than that shown on Fig. 2. Neither type is as steady here as when it exists by itself alone. As the current increases, the trains of waves from Type B become longer and the intervals (Type A) shorter, until at 1.73 amp. (Fig. 2) Ring A ceases altogether and Ring B alone is seen. Direct examination with the rotating mirror reveals the same effect. The data for Fig. 2 are not taken from the films shown in Fig. 3.

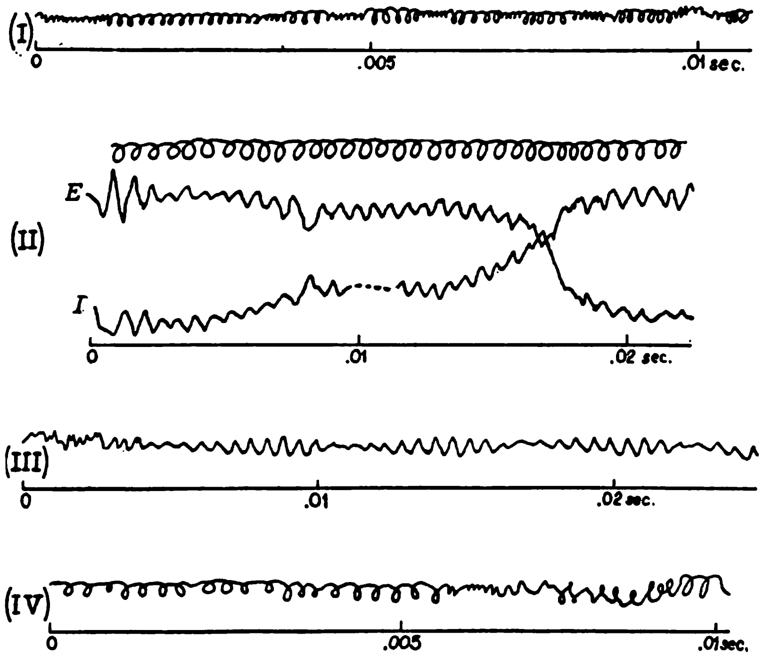

Fig. 3.

I. Photograph of positive base on moving film. Types A (large) and B (small) alternating. Mean diameter of ring, Type A, 0.3 mm. Current, 1.75 amp.

II. Oscillograph records of p.d. and current, together with image of positive base similar to (*I*). Type C, frequency 1,600. In *E* curve, 1 mm. = 1.34 volts; in *I* curve, 1 mm. = 0.013 amp. Diameter of ring, 0.9 mm. Current, 2.05 amp.

III. Oscillograph record of p.d., Type C, frequency 1,670. 1 mm. = 1.23 volts.

IV. Photograph of positive base, Type D. 1 mm. = 0.206 mm. at anode of arc. Current, 2.75 amp.

The audible pitch falls gradually in a peculiar manner while the transition from Type A to Type B is in progress. This, I think, is due to slowing down of the column of entrained gas, which, as long as Type B alternates with Type A, fails to keep in step with either ring. The sound of course proceeds from the moving vapor and not alone from the positive base of the arc.

§ 6. *Type C.*—On the film on which Fig. 2 is based, Type B lasts only up to 1.80 amperes, when quite suddenly it gives place to the third type. Here the diameter is much larger and the frequency correspondingly lower. This, by far the most conspicuous of the rotations, is the one referred to in the earlier papers. Occasionally Type C fails to appear, or at most it comes in a few irregular trains. This is especially the case when the arc is disturbed or when the gas contains an insufficient supply of oxygen. The range of current over which Type C prevails is often very limited, in the present case only from 1.80 to 1.88 amp. Under normal conditions, Type C begins at about 2 amperes and lasts until 2.3, or even 2.5, amperes, at which point Type D begins.

The audible tone due to Type C, which may be heard at a considerable distance from the arc, varies in the manner indicated by the frequency curve in Fig. 2. The absolute values of f and δ are nearly the same, at whatever current the ring first appears.

In Fig. 4 may be seen a charcoal drawing of the arc between an iron anode and carbon cathode, based upon a photograph. Owing to very unequal light distribution, the photograph did not lend itself to direct reproduction. The diameter of Ring C was 0.91 mm., current 2.12 amp.

Simultaneous records of current and voltage, together with the image of the positive base for Type C, are shown in the second group of curves, Fig. 3. The long-period fluctuations in the oscillographic records, which are very evident on the complete film (only a part of which is here shown), are due either to swaying of the arc or to wandering of the negative base. Whatever the cause, it is evident that the movement of the positive base was undisturbed. Curve *III* of Fig. 3 is a voltage record for Type C, showing irregular fluctuations at the beginning, as well as the appearance of beats (cf. § 10).

§ 7. *Type D.*—At 1.88 amp. the film under discussion shows a sudden change to the fourth type of rotation, Type D. This, the final type, lasts in air at atmospheric pressure up to about 5 amp. The frequency falls and the diameter increases with increasing current (Fig. 2). Beyond 3 amp., however, the motion becomes very irregular. Still, up to 5 amp. the rotating mirror still shows detached trains of large waves in the midst of the irregular wandering of the positive base; at about this point the movement ceases somewhat suddenly, as explained in § 22. From then on, no tendency to wander has hitherto been observed.

The appearance of Ring D, as revealed by the moving film, is seen in Curve *IV* of Fig. 3. The disturbed state characteristic of large currents is here in evidence.

As has been stated, the currents for this particular film were smaller than those usually encountered. In general, one may look for the four types at about the following values of current: Type A, from 1.4 to 1.8 amp.; Type B, from 1.8 to 2.0 amp.; Type C, from 2.0 to 2.5 amp., though very often Type B or Type D encroaches widely on this interval; Type D, from 2.5 to 5 amp.

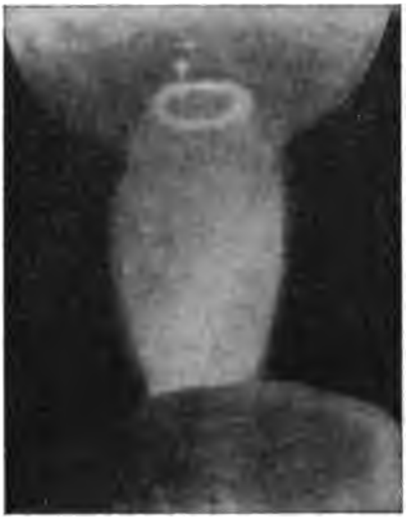

Fig. 4.

Iron arc rotations, Type C. Below: Carbon cathode. Above: Iron oxide anode. Current, 2.12 amp. Diameter of ring, 0.91 mm.

§ 8. *Remarks on Type C.*—The vapor of the arc for a distance of several millimeters from the anode seems to partake of the motion. At any rate, the arc becomes diffuse, and the envelope of yellow flame surrounding it, which is due chiefly to the oxidation of the iron vapor, flickers convulsively the moment the ring appears. If the arc is shortened to about 2.5 mm., the negative base is also affected by the rotation and the anode ring is less distinct. With still shorter arcs, Type C fails to appear, though the other types are still in evidence. It would appear from this that only about 2.5 to 3 mm. of vapor, at the anode end of the arc, is affected by Type C, and that the vapor is even less influenced by the other types. Type C generally passes through a very disturbed state at largest currents, just before the change to Type D takes place. Sometimes the arc appears to divide into two or more parallel arcs. The anode sometimes becomes so cooled at such times that in spite of the large current the change from second to first stage (non-vaporizing anode) occurs. Over this part of the characteristic curve accurate observations of current and p.d. are impossible.

On diminishing the current, the observations on all four rings are repeated in reverse order. Whenever Type C begins, whether on increasing or decreasing current, the drop across the arc always increases 1 to 2 volts while the current decreases slightly. This is probably due to the lengthening of the arc.

The tendency of both ends of the arc to wander over the surfaces of the electrodes is a most exasperating feature of the work, rendering precise observations utterly impossible. Various remedies, such as steadying the arc by holding a bar magnet near it, have been tried without success. Ring C is the hardest form to obtain. It is seen generally only for a few seconds at a time, though under good conditions it may last a full minute.

§ 9. *Refraction of Light by the Column of Hot Vapor.*—The surface of the iron oxid globule, which under normal conditions is brightly incandescent, is extremely smooth, giving a distinct reflected image of the column of vapor and of the negative end of the arc, especially when a carbon cathode is used. If the globule is viewed from such an angle that the negative crater is reflected from a point near the positive base of the arc, a curious distortion takes place: the image sends out a line pointing toward the positive base, and sometimes a second fainter image appears close to the main one, in a direction away from the positive base. This condition is shown close to the ring in Fig. 4.

The first of these effects is probably due to refraction of the light from the crater by the hot vapor of the arc. The second image seems to result from a deformation of the surface of the globule, caused by the mechanical pressure which the arc is known to exert upon the molten surface.

No distortion of the image of the negative crater is seen on the first stage of the arc, as the positive base is then very diffuse and no vaporization of the anode takes place.

A similar distortion of the reflected image was observed with anodes of other metals and oxides (§ 26).

§ 10. *Observations with the Oscillograph.*—It seemed desirable to study the variations in voltage and current produced by the rotations. A Duddell high-frequency oscillograph with rapidly moving film was used. In some cases an image of the anode of the arc was projected on to the film, in addition to the oscillograph spots. A part of one such record is shown in Fig. 3, *II*.

Owing to the high frequencies involved, it was not possible to secure oscillographic records showing accurately the wave-form of the current and voltage curves. Indeed, except at the lowest frequencies, variations accompanying Types A, B and D could not be seen at all. Type C was always found to be accompanied by oscillations in arc voltage amounting to ± 1 to 3 volts, and in current amounting to ± 0.01 to 0.03 amperes. The cause of these fluctuations lies probably in periodic changes in length and temperature of the arc, especially since in taking the photographs the electrodes were moved out of vertical alignment in order to bring the positive base as far over on to the side of the globule as possible.

On some films the amplitude of the oscillograph curves varies periodically, reaching a minimum every ten to twenty cycles, or even passing through a zero value and suffering a phase displacement of 180°, as in Fig. 3, *III*. This at once suggests beats, and indeed it is not impossible that such were present, since once in a while two tones could be heard at once during Type C. The appearance of beats, moreover, would be produced if, owing to air currents or other cause, the entire ring swayed from side to side over the surface of the globule. Direct evidence of such swaying was sometimes furnished by the blurred appearance of the ring. This might account for the production of two musical notes, especially through the action of the Doppler effect.

On the whole, the determination of current and voltage relations does not seem to be of particular value in the study of these rotations, except in so far as it throws additional light upon the periodicity. These observations with the oscillograph serve, however, to explain the nature of the oscillations in the iron arc current which Arnold and the writer[1] found always to be present on the second stage.

Self-inductances (transformer windings) were at times connected in series with the arc on both sides, but they were without effect upon the period or sound of the rotations.

THEORY OF THE ROTATIONS.

§ 11. It is well known that in both glow and arc discharge, rotation of the positive column can be produced by a radial magnetic field. It is conceivable that in the present case, a magnetic field perpendicular to the plane of the ring might maintain the circular motion by virtue of its component at right angles to the arc stream. The writer thought at one time that this would prove to be the cause of the rotations. That such is not the case became clear when it was found that the period and amplitude of the rotations are independent of the direction of the arc in space, and that the direction of rotation often reverses itself spontaneously. Moreover, I have placed the arc in a magnetic field whose direction and intensity were varied through wide limits, without detecting the slightest influence on the rotations.

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[1] Cady and Arnold, *l. c.*, pp. 405, 409.

Dufour[1] found that the irregular wandering of the cathode base of the mercury arc, caused by excess of vapor pressure, can be made to resolve itself into a circular motion. This cannot, however, be the controlling cause of the iron arc rotations, since, as will be seen (§ 24), the presence of oxygen is the prime requisite for their maintenance.

Trotter[2] observed a rotation of the bright spot at the anode of the carbon arc just before the beginning of the hissing stage. This was later shown to be due to the inrush of oxygen into the crater.[3] As will be seen (§ 15), this bears a closer resemblance to the present rotations than any of the other types hitherto known.

§ 12. It seems most probable that the rotations here described find their origin in modifications in the composition of the globule of oxid at the anode. We will consider first the cause of the wandering of the positive base, and then the conditions necessary for the maintenance of a continuous rotation.

As has been stated, the anode globule on cooling is found to consist of magnetic iron oxid, $FeO.Fe_2O_3$. This oxid is known to possess a complex structure, and to undergo changes in its physical properties at certain critical temperatures.[4]

Walden[5] found Fe_2O_3 to be stable in air up to about 1350° C., at which temperature it dissociates into O and Fe_3O_4. Kohlmeyer,[6] on the other hand, assigns to the melting point of Fe_2O_3 the value 1565°, with transition points at 1300° and 1035°. Hilpert[7] calls attention to the influence of previous history and method of treatment on the dissociation temperature of Fe_2O_3, while Wüst[8] asserts that at 1050° the compound $FeO.Fe_2O_3$ is formed, at 1100° $2FeO.Fe_2O_3$, and at 1200° $3FeO.Fe_2O_3$. According to Hilpert, Kauffmann identified also $2FeO.3Fe_2O_3$. I know of no investigations on the reactions that take place at higher temperatures than these, but it seems not improbable that still others occur before the final reduction of the iron is accomplished. In addition, there is the possibility of the formation and dissociation of a nitride.

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[1] Dufour, Jour. Phys., 5th Ser., 1, p. 109, 1911.

[2] Trotter, Electrician, 33, p. 298, 1894.

[3] Mrs. Ayrton, The Electric Arc, p. 300.

[4] *Cf.* Heaps, Phil. Mag., 24, p. 813, 1912. Somerville, PHYS. REV., 34, p. 311, 1912. Koenigsberger, Phys. Zeitschr., 13, p. 282, 1912.

[5] Walden, Jour. Amer. Chem. Soc., 30, p. 1350, 1908.

[6] Kohlmeyer, Metallurgie, 6, p. 323, 1909.

[7] Hilpert, Ber. Deutsch. Chem. Ges., 42, p. 4893, 1909.

[8] Wüst, Metallurgie, 5, p. 11, 1908.

Apparently at any given gas pressure the temperature close to the positive base of the iron arc is determined solely by the current. At any rate, heating the rod to which the positive globule is attached does not perceptibly affect the rotations.

§ 13. *Temperature of the Anode Globule.*—A Pt : PtRh thermo-element was thrust into the molten globule after the arc had been started, and observations for temperature were made at various values of the arc current. Owing to the wandering of the arc and the turbulence of the molten oxids, the results were very irregular, but the mean temperature of the globule seemed to be in the neighborhood of 1600° C. for currents between 1.5 and 3 amp. Close to the positive base of the arc the platinum wire melted, and this occurred also when the thermo-element was thrust deeply into the globule to a point about one millimeter below the positive base, showing that here also the temperature is very high. Where the oxid touched the iron rod on which it rested, its temperature must of course have been below the melting point of iron, 1530°; half-way up the side of the globule the temperature was about 1450°, at a current of three amperes. The globule was about 4 mm. in diameter.

The relative brightness of different parts of the surface of the globule was observed by projecting an enlarged image of the globule onto the screen of a photometer, the other side of which was illuminated uniformly by an incandescent lamp. No estimate of the actual temperature by this method was attempted, because the emissivity of the oxids is not known. But it was evident that the surface temperature fell off considerably as the distance from the positive base increased, and as the current decreased, as was to be expected.

From these tests it is clear that in the neighborhood of the positive base the temperature is so high that it is impossible to conjecture what compounds may be present there. At the positive base itself the material may be reduced iron at all currents (except, of course, on the first stage). No conclusion as to the nature of the positive base can be drawn from an examination of the globule after it has cooled, for even in the absence of oxygen, as soon as the arc is put out, diffusion quickly removes all traces of the positive base. I tried quenching the globule suddenly with mercury on the instant of opening the switch in the arc circuit, but found that the globule flew to pieces on contact with the cold mercury.

§ 14. From the above considerations it is apparent that at any given current the compounds in the region immediately surrounding the positive base of the iron oxid arc are richer in oxygen than is the positive base itself. If the arc took place with the same ease from all these compounds, and from pure iron itself, there would be no tendency for the positive base to wander. In a preliminary communication,[1] the view was expressed that the positive base was more highly oxidized than the surrounding region, and that the cause of the rotations lay in a higher anode drop at this point. More recent experiments[2] have indicated, on the contrary, that the lower drop which seemed to be present when the anode was of metallic iron was due to the arc vapor rather than to the anode, and that in fact the arc takes place with greater ease from an oxidized anode. Hagenbach[3] has recently found the anode drop to be less from an oxidized anode than from the pure metal. Whether the tendency of the arc to burn from the oxids rather than from pure iron is due to a specific property of the oxids or to their lower boiling points cannot at present be determined. It is exceedingly difficult to obtain reliable values of the anode drop with an exploring electrode, owing to the small size and instability of the arc at the small currents in question.

It was found by Stark and Cassuto[3] that the anode drop in the arc increased with increasing temperature. If this is true of the iron oxid arc, it may furnish the reason why Hagenbach found the anode drop less from oxids.

The physical and chemical processes attending the progressive reduction and vaporization of the oxids may of themselves increase the ionization in the arc and thus lower the potential gradient.[4]

For these reasons, the following discussion is based on the hypothesis that the anode drop, owing to the reduction of the positive base, is somewhat higher than it would be if the arc could take place from the more oxidized surrounding region.

§ 15. It follows from the foregoing section that if the positive base chances to move slightly, the drop at its advancing edge is less than that over the rest of its surface, hence the motion continues along a more or less regular path.

The propelling force may be expressed thus:

$$F_1 = k_1(P - P'), \tag{1}$$

where P is the value of the drop at the reduced positive base, P' that for the region immediately surrounding, and k_1 is a function of the current.

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[1] Phys. Rev., 35, p. 77, 1912.

[2] Phys. Zeitschr., 14, p. 296, 1913.

[3] Hagenbach, Phys. Zeitschr., 12, p. 1019, 1911.

[4] Stark and Cassuto, Phys. Zeitschr., 5, p. 264, 1904.

[5] *Cf.* Child, Electric Arcs, New York, 1913, p. 181.

After the motion has become established, F_1 does not necessarily lie in the same direction as the velocity.

Herein lies the most reasonable explanation of the movement of the positive base. A similar view has been advanced by Wagner[1] to account for the irregular wandering at the cathode in the aluminum arc.

After the movement has once begun, the inrush of oxygen into the wake of the arc, combining with the reduced iron, may serve as an additional component of the propelling force.

§ 16. *The Production of Stable Rotations.*—The relations between the forces that control the rotations are shown in Fig. 5. In this figure O is the undisturbed position of the positive base, and Q its position at any time t. Then the movement of the base will be determined by the following forces: F_1 the propelling force, which makes an angle α with the radius vector produced; F_2 the central force (§ 17); and F_3 a resisting force which acts in a direction opposed to the element of path ds. F_3 arises partly from the resistance offered by the surrounding air to the motion of the column of vapor, partly from the fact that the advancing arc must raise the temperature of the positive base to vaporization. It must therefore increase as the velocity increases.

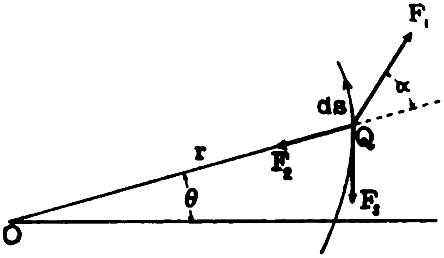

Fig. 5.

The equations of motion are as follows:

$$m\left[\frac{d^2r}{dt^2} - r\left(\frac{d\theta}{dt}\right)^2\right] = F_1\cos\alpha - F_2 - F_3\frac{dr}{ds}, \qquad (2)$$

$$m\left[\frac{1}{r}\frac{d}{dt}\left(r^2\frac{d\theta}{dt}\right)\right] = F_1\sin\alpha - F_3\frac{rd\theta}{ds}. \qquad (3)$$

From the nature of the phenomenon, it is impossible to express α as a simple function. Still it is certain that α tends to diminish as the distance $r = OQ$ decreases, for near the center the temperature is highest and the globule most reduced, hence that edge of the positive base that is farthest from the center will possess a lower anode drop than the nearer edge. This must tend to direct F_1 more strongly away from the center when r is small. The consequence of this will be to widen out the orbit into a circle. Thus if the positive base moves at all, *the motion must speedily resolve itself into a circular orbit with constant velocity.*

§ 17. In order to investigate the central force F_2, several series of observations were made, in which the positive base of the arc was deflected by a magnetic field of known magnitude. Values of field intensity between 0.6 and 7 c.g.s. units were employed. The position of the negative base of the arc at the carbon cathode remained unchanged, the entire arc turning slightly around it as a center when the field was applied, keeping its form unaltered. In this way the stability of the arc against displacing forces could be studied, both when the rotations were present (in free air), and when they were absent (in absence of oxygen, see § 24). Since nearly the same magnetic deflections were obtained in each case, it seems fair to assume that in the rotations the positive base is subject to a restoring force, directed toward the center of the ring, obeying the same laws, at least qualitatively, as those derived from the magnetic experiments.

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[1] Wagner, Der Lichtbogen als Wechselstromerzeuger, Leipzig, 1910, p. 90.

It is unnecessary to state the details of these experiments. As a result of them I found that for arc currents I between 2 and 4 amperes, and length l of arc from 3.5 to 9 mm., the restoring force F_2, expressed as a force in dynes acting on the positive base when the latter is displaced r cm. from its original position, is given approximately by the empirical equation

$$F_2 = \frac{Ilr}{(0.26l - 0.64) - (0.032l - 0.096)I}. \tag{4}$$

For currents less than 2 amp., and also, curiously enough, for Type C, the value of F_2 is slightly larger than that derived from eq. (4). This equation is, moreover, not accurately applicable to the rotations, since in them only a part of the entire length of arc is affected, so that the effective value of l is not known. For the present paper it is enough to point out that F_2 varies directly as the radius, and hence as the diameter δ of the ring, and that it also increases as the current increases. For constant current and length, eq. (4) may be simplified thus:

$$F_2 = k_2\delta, \tag{5}$$

in which k_2 is a constant.

§ 18. In what follows it will be assumed that the motion of the positive base has reached a steady state, the orbit being a circle of definite diameter and period, and the velocity being constant. The equations of motion (2) and (3), § 16, are now reduced to

$$-mr\left(\frac{d\theta}{dt}\right)^2 = F_1 \cos\alpha - F_2,$$

and

$$0 = F_1 \sin\alpha - F_3.$$

In the first of these equations we will put the normal acceleration a in place of $r(d\theta/dt)^2$, and then obtain with the aid of eq. (1), § 15:

$$a = \frac{F_2 - F_1 \cos \alpha}{m} = \frac{F_2 - k_1(P - P') \cos \alpha}{m}. \qquad (6)$$

It has been shown that the retarding force F_3 increases with the velocity. If we write $F_3 = k_3 v$, we obtain from the second equation above:

$$v = \frac{F_1 \sin \alpha}{k_3} = \frac{k_1(P - P') \sin \alpha}{k_3}. \qquad (7)$$

Since $F_1 \cos \alpha$ is finite, while F_2 is a central force varying directly as the distance, it is clear that the condition for stable circular motion is satisfied.

§ 19. The four types of rotation may now be studied in the light of equations (6) and (7). In Fig. 2 were shown the changes in frequency f and diameter δ of the rings with increasing current. From these, the curves in the lower part of Fig. 2 have been constructed, showing the linear velocity and normal acceleration. The values of v and a were derived from the equations

$$v = \pi \delta f$$

and

$$a = 2\pi^2 f^2 \delta.$$

The most striking conclusion to be drawn from the curves is, that the changes from ring to ring are due almost entirely to changes in normal acceleration. The linear velocity remains remarkably constant throughout.

For Types A, B and D, the observed decrease in a as the current increases may be ascribed to the increase in the mass m, though it must be remembered that F_2, k_1 and k_3 also are functions of the current.

Let us consider the transitions from one type of rotation to the next. On passing from Type A to Type B, a increases and δ decreases, hence F_2 decreases (eq. 5, § 17), and $F_1 \cos \alpha$ decreases *à fortiori* (eq. 6). Since at the same time v increases slightly (Fig. 2), it must be that α increases also (eq. 7). Thus in Type B the propelling force would seem to be less than in Type A, and to be directed more nearly parallel with the path. The decrease in F_1 must be due to an increase in P', the anode drop characteristic of the region surrounding the positive base. In other words, a modification in the composition of the oxid occurs here.

Between Types B and C, a decreases and δ increases, hence F_2 increases, as does also $F_1 \cos \alpha$. Unless the resisting force F_3 were greatly changed, this would be expected to make v increase. Instead, v is diminished, indicating a decrease in the value of α. In Type C, therefore, the propelling force F_1 seems to be very large and to have a pronounced radial component.

§ 20. Type C, while the most conspicuous when it appears, is also the most puzzling. It ceases altogether in an atmosphere of illuminating gas or of nitrogen, though the other types persist until the reduction of the oxid proceeds too far for their continuance. Free oxygen in the gas around the arc seems essential to the existence of Type C. Possibly at a certain critical temperature there is a sudden inrush of oxygen around the base of the arc, lowering the drop in the region close to the positive base and thus greatly increasing F_1 (cf. § 24). A further increase in current may bring about a more complete reduction of this surrounding region, so that the original condition is restored. This will have to remain mere conjecture until more is known of the oxids of iron at high temperatures. At any rate, the agitated appearance of the arc during Type C is favorable to such an hypothesis.

A careful examination of the spectrum of the arc before, during and after the appearance of Ring C failed to reveal any changes in the prominent lines of iron, oxygen, carbon, or nitrogen other than a gradual brightening as the current increased.

The cause of the changes in Ring C with increasing current seems to be essentially the same as for Ring A.

§ 21. Type D would appear to be a continuation of Type B if it were not for Type C. Indeed, it may be, as suggested above, that Type C is interjected in the midst of a single type of rotations to which both B and D belong. Type D seems governed by the same laws as Type B. The lack of agreement in the values of v in Fig. 2 results chiefly from the difficulty in determining the diameter. The rings are so minute that measurements on the photographic film were very difficult.

§ 22. *Lengthening the arc* from 3 to 6 mm. causes the frequency of Type C to decrease from 5 to 10 per cent., that of Type A to decrease at a somewhat greater rate. A dependence of the frequency of Types B and D upon the length has not been determined.

The change in frequency follows directly from the observed decrease in F_2 as the length increases (eq. 4, § 17). The fact that the dependence of frequency upon length is slighter than would be expected from eq. 4 is added evidence that only a part of the entire length of arc is affected by the oscillations.

Reference has been made (§ 7) to the cessation of the rotations at about five amperes. This takes place somewhat abruptly, the diameter of Ring D increasing not only up to 3 amp., as shown in Fig. 2, but beyond this: as long as the positive base continues in motion, the amplitude of its movement increases, although the form of the ring becomes indistinguishable between 3 and 4 amp. It may be that the positive base is surrounded with a zone of reduced iron which increases in width as the current increases. As long as the current is not too large, the positive base pushes across this zone on one side, and the movement is maintained. But at a certain critical current, in this case about 5 amp., the reduced zone attains such a width that the positive base fails to cross it any longer. The rotations then immediately cease, except for a few last convulsive movements that can generally be observed.

§ 23. *Conditions at the Cathode.*—When the cathode consists of a globule of iron oxid, no rotations are ever observed except when the arc is so short that the negative base is influenced directly by the rotations at the anode. One would suppose from Wehnelt's investigations that the cathode drop must be lowered at least as much as the anode drop by the presence of oxid. It may be, however, that even at small currents the cathode temperature is so high that a zone surrounding the negative base is reduced to the same degree as the negative base itself. The fact that the negative terminal of the iron arc always wastes away much faster than the positive is in agreement with this hypothesis.

There is also a quite different possibility that ought not to be disregarded, if it is true of iron oxid[1] as it is known to be true of certain other oxids in the molten state, that the substance conducts electrolytically. For in this case, as the current passes through the molten negative globule, there must be a transfer of oxygen ions to the negative base of the arc. The amount of oxygen liberated in this way by purely electrolytic conduction would amount, if two amperes flowed for five minutes, to 0.05 gram. Hence if the conduction is to any considerable degree electrolytic, there may well be a sufficient supply of oxygen near the negative base of the arc, to hold the cathode drop at a minimum value. No data are at present available for deciding between these two hypotheses.

At the anode, on the other hand, the contrary would take place if the oxid conducted electrolytically. The positive base would become depleted of its oxygen, thus increasing the reduction of the iron, and raising the anode drop.

OBSERVATIONS WITH OTHER GASES AND ANODE METALS.

§ 24. *Effect of Reducing the Amount of Oxygen in the Gas Around the Arc.*—The arc burned in air at atmospheric pressure, but the front of the tube was closed by a glass window so that the oxygen gradually became exhausted, chiefly by combination with the carbon that served as cathode. The following changes took place:

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[1] Rasch, Phys. Zeitschr., 5, p. 375, 1904.

All four types of rotation came at *larger* currents than usual. This was probably due in part at least to the fact that the globule was cooler and less plastic than in free air, and the positive base less concentrated, thus requiring a greater current to produce the conditions necessary for rotations. As the reduction proceeded, Type C was the first to cease, then Type A, while Types B and D seemed to merge together. Then for a time only Type D existed, continuing up to a current of about ten amperes; and after prolonged burning, the globule was so far reduced that no rotations whatever could be detected.

These facts all agree with the theory that the rotations are due to different oxids, and that Type D represents the oxid of lowest oxygen content.

Opposite effects were produced when a current of oxygen was allowed to play gently around the arc in air. The appearance of Type C came at a *smaller* current, for example, than under normal conditions.

Observations of magnetic deflections (§ 17) in air deficient in oxygen showed that the central force F_2 is of approximately the same magnitude when the oxygen is exhausted and no rotations are present, as in normal air.

§ 25. *Observations in Air at Reduced Pressure.*—The discharge tube was connected to a water aspirator, and observations made at various pressures between atmospheric and 420 mm. of mercury. In order to keep up the supply of oxygen, a slow current of air was allowed to be drawn through the tube, the rate of flow being so regulated as to hold the pressure at the desired value. In spite of this, the globule became somewhat reduced, so that the observed changes were in part due to lack of sufficient oxygen.

The changes observed with Types A, B and D were practically the same as at atmospheric pressure with deficient supply of oxygen, and the same reasoning is doubtless applicable to this case also. Type C on the other hand behaves quite differently. A decrease in pressure is followed instantly by a lowering of the pitch. A larger and larger current is required to introduce Type C, until at 420 mm. the current is 4.5 amp., frequency 385 (the lowest I have recorded), and diameter of ring is greatly increased. The normal acceleration is evidently greatly diminished at reduced pressure.

This is the more surprising, since there is evidence from magnetic observations at low pressure that the central force F_2 *increases* slightly as the pressure is lowered. It must be that the outwardly directed component of the propelling force increases greatly as the pressure decreases.

One would expect that a reduction of the gas pressure would lower the temperature of dissociation of the oxids, and thus cause the rotations to come at a smaller current. Thus Walden[1] finds that the dissociation temperature of Fe_3O_4 is about thirty degrees lower at 420 mm. than at atmospheric pressure. On the other hand, we must remember that at low pressure the globule is cooler, the positive base more diffuse, and that the positive drop is probably less than at atmospheric pressure.[2]

§ 26. *Tests with Other Metals.*—In conclusion, brief mention may be made of attempts to obtain the rotations with anodes of other materials than iron oxid. Only those substances were used that form fairly regular liquid globules. In most cases the cathode consisted of carbon. The anode was either in the form of a rod, or a pellet resting on a carbon holder.

Nickel.—After the anode had become oxidized, the positive base of the arc showed much agitation at currents between 2 and 5 amp. No ring could be seen, but the rotating mirror revealed irregular periodic movements of frequency ranging between 400 and 4,000. As in the case of Type D of the iron arc rotations, the frequency became less as the current increased.

In the neighborhood of 1.4 amp., the arc from a nickel oxide anode presents an extraordinary appearance. Two or three arcs seem to spring into being, all moving rapidly about, while in the telephone (§ 3) a strange medley of musical notes, covering a range of two octaves, is heard.

Cobalt.—Between 1.4 and 1.75 amp. the positive base is agitated and a soft shrill whistle can at times be heard. The rotating mirror shows irregular groups of waves of about the same size as those in Type C of the iron arc. The anode was always oxidized.

These facts all point to processes in the nickel and cobalt arcs similar to those in the iron arc, though the globule at the anode is evidently too little homogeneous, or conditions are otherwise too unfavorable, for the formation of steady rotations.

Copper.—No periodic movement of the positive base could be detected, though the arc often moved about irregularly, as is the case with any arc at small currents. When the copper oxid anode is in the form of a bead resting on a carbon holder, it often falls into a condition like the spheroidal state, owing to imperfect thermal contact with the carbon. At such times a faint humming note is sometimes heard. Still, there is no evidence that at the anode of the copper oxid arc there are forces of the same nature as those in the case of iron.

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[1] Walden, Jour. Amer. Chem. Soc., 30, p. 1350, 1908.

[2] Cf. Child, this journal, 19, p. 129, 1904.

Silver.—Though the silver does not oxidize, its behavior on a carbon holder is much like that of copper oxid. The positive base moves about continually, but its motion is comparatively slow, and there is absolutely no sign of such forces as produce the rotations.

Tin.—A white, fleecy oxid soon forms in air, but the arc prefers to burn from the molten metal rather than from this oxid, and there is no sign of any unusual movement.

Mercury.—The carbon cathode became red hot, even with a current as low as 0.5 ampere. The positive base seemed quite stationary, the arc burning from the metal, not from the oxid that formed; then after a few seconds it sprang suddenly to a new position on the surface of the mercury, and kept this process up at intervals as long as the arc burned. A high-pitched note was often heard. The arc formed a narrow column of vapor at right angles to the mercury surface, extending almost to the cathode, where it bent abruptly and continued for a short distance almost parallel to the surface of the cathode, finally ending at a bright spot on the carbon. This is mentioned because, whenever the note was heard, the vapor in the neighborhood of the *cathode* seemed agitated, as if the sound proceeded from it rather than from the anode.

From these experiments it seems clear that forces at the anode of the arc, tending to keep the positive base in a circular motion, are possible only when the anode consists of certain metallic oxids in a smooth and molten state.

My thanks are due to Messrs. A. C. Stevens, H. P. Frost and F. H. Frame, by whom many of the observations recorded above were obtained.

SUMMARY.

The arc in air from an oxidized iron anode exhibits, under normal conditions, four types of rotation, which are called for convenience Types A, B, C and D. They occur in succession as the current is increased from about 1.5 to 2.5 amp., though Type D generally lasts up to about 5 amp. The characteristic features of each type, including its frequency, amplitude, and appearance, are described, and photographic records of the movements at the anode, together with the accompanying fluctuations in voltage and current, are shown.

Reasons are given for believing that these rotations owe their existence to a difference between the potential drop at the positive base of the arc and that characteristic of the surrounding region. At the positive base,

the oxid is more reduced and the potential drop is therefore greater; the high temperature probably enhances the effect still further.

In §§ 15 and 16 the conditions for the production of stable rotations are discussed, and in § 18 equations of motion of the positive base are derived. A comparison of these equations with the observed data throws some light on the nature of the forces acting on the arc. A more complete discussion of the dynamics of the rotations cannot be carried out, owing to the impossibility of securing sufficient data. The very high temperature of the arc makes it impossible to determine what oxids are at or near the positive base.

Observations with other metals and in other gases tend in the main to confirm the conclusions reached with iron oxid. Oxids of nickel and cobalt show some evidence of forces similar to those in the iron arc.

In conclusion, a word may be said concerning the proposal made at the recent conference of the International Union for Coöperation in Solar Research, that for the production of reference spectra of wave-length less than 4,000, the iron arc with a current of four amperes or less be used. As we have seen, at all currents less than five, rotations of some one of the four types generally occur when the iron arc burns in air. As the discharge passes from one type to the next, one would not expect the slight changes in the oxid at the anode to have any effect on the spectrum of the iron vapor. The writer, using a grating of medium resolving power, could not visually detect any characteristic change in the spectrum when the arc passed through Type C. Still, it would seem desirable, before adopting as standard the iron arc at small currents, to be quite sure on this point. Moreover, the fact that a part of the column of vapor is in motion during the rotations makes it somewhat difficult to use any restricted portion of the arc as source of light. This is especially true when the current lies between 2 and 2.5 amperes (Type C). By letting the arc burn in a gas that is sufficiently deficient in oxygen, however, the rotations can be entirely eliminated (§ 24).

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A DIRECT METHOD OF FINDING THE VALUE OF MATERIALS AS SOUND ABSORBERS.

By Hawley O. Taylor.

THE sound-absorbing quality of materials has been recognized for some time as having an important bearing upon architectural acoustics. In 1873, T. Roger Smith, M.R.I.B.A., a leading British architect, wrote:[1]

"Where there is too much resonance in a room, carpets or curtains may be advantageously employed to lessen it; in fact, to absorb the injurious excess of sound, and where there is an echo, a curtain judiciously hung will have the effect of deadening or stopping the sound before reaching the echoing surface. This expedient is well known, and often successfully employed; but carpets, as a remedy for excessive resonance, have perhaps not been so frequently made use of."

Since 1895, extensive investigations have been carried on at Harvard University by Professor Wallace C. Sabine[2] to determine some quantitative relations between the size, reverberation and sound-absorbing power of a room, and he placed his results in the well-known form:

$$a = \frac{.171\,V}{t},$$

where a is the absorbing power of a room of volume V, and t is the time of decay of the residual sound of an organ pipe whose intensity in terms of "minimum audibility" had been previously determined. As determined by Sabine, a room is most satisfactory for speaking purposes when t has a value of about 1.5 seconds, thus the proper amount of absorbing power, a, is limited. (The above equation does not apply to echoes and defects due to the shape of a room.) Since the sound-absorbing power of an auditorium is thus limited to a narrow range of values, the consideration of absorption is of great importance in auditorium design and construction.

The amount of absorption is equal to the sum of the absorbing powers of the different materials composing the bounding surfaces and the furniture of the room; the absorbing power of the material is equal to the product of its area and the amount of sound absorbed by unit area. Sabine rated the amount of sound absorbed by unit area of open window as 1, then the amount absorbed by a material which reflects a part of it is always less than 1. This fraction is the coefficient of absorption of sound for a given material.

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[1] T. Roger Smith, "Acoustics of Public Buildings," p. 39.

[2] Prof. W. C. Sabine, Am. Arch., Vol. LXVIII., April 7, 21, May 5, 12, 26, June 9, 16, 1900.

Besides the power of materials to absorb sound reflected from their surfaces, it is desirable also to know the power of materials to absorb sound transmitted through them. The application of this to architecture extends beyond the acoustics of a single room and has to do with the isolation of one room from sounds produced in another. The interior finish of rooms is of no consequence here, but the filling in the partitions and in the space under the floors is the important thing. The fraction of sound absorbed by unit thickness of a given material may be called the coefficient of absorption of the material for transmitted sound, or the insulation coefficient of the material for sound.

To find the coefficient of absorption of a material for sound reflected from it the method usually employed is to bring a known amount of the material in question into a room and make observations for the time of decay of the residual sound, applying the formula above stated. This may be called the reverberation method. The purpose of this investigation is to devise a direct method of finding the coefficient of absorption of materials for sound. Such a method is formulated and following is the theoretical basis:

When a train of progressive waves, P (Fig. 1), of amplitude, p, moves in the positive direction, say, then all points of the medium in the path of the waves move through a distance $2p$, as shown by the shaded portion of Fig. 1.

If the progressive waves strike an object, S (Fig. 2), and a portion of each is reflected, these reflected waves, R, of amplitude, r, will travel in the negative direction, and the two trains of waves will meet and combine. Some points of the medium will then move through a greater and others through a less distance than before, as shown by the shading in Fig. 2. The maximum amplitude (where crest meets crest and trough meets trough) will be $p + r$, and the minimum amplitude (where the crests of P meet the troughs of R, and vice versa) will be $p - r$.

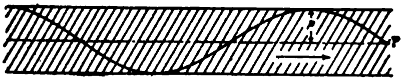

Fig. 1.

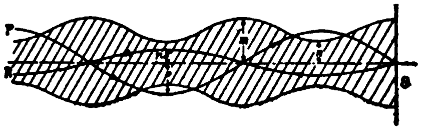

Fig. 2.

A special case of this phenomenon is when the progressive and reflected waves have the same amplitude, p. The resultant maximum amplitude is then $2p$, and the minimum amplitude is zero. This is the ordinary stationary or standing wave. In order to have no motion at the nodes the two waves must be equal in amplitude, which is only the case when there is no absorption at the reflecting surface.

The distance through which the medium moves varies from point to point, as represented by the amplitude of the envelope in Fig. 2. In the case of sound waves, this movement is the longitudinal vibration of the air particles, the intensity of the sound being greatest where the amplitude of vibration is greatest. The coefficient of absorption of sound is a function of sound intensity and therefore of the squares of the amplitudes of the progressive and reflected waves and of the resultant stationary wave (the envelope, Fig. 2). The intensity of sound in the progressive wave is $(kp)^2$, and the intensity of sound in the reflected wave is $(kr)^2$ (where k is a proportionality constant). This gives a coefficient of reflection,

$$\rho = \frac{r^2}{p^2}.$$

If the maximum intensity of sound (corresponding to the maximum amplitude of the envelope, Fig. 2) is called m, and the minimum intensity (corresponding to the minimum amplitude of the same envelope) is called n, then

$$m = (p + r)^2,$$

$$n = (p - r)^2,$$

from which

$$p = \frac{m^{\frac{1}{2}} + n^{\frac{1}{2}}}{2},$$

$$r = \frac{m^{\frac{1}{2}} - n^{\frac{1}{2}}}{2}.$$

Substituting these expressions for p and r in that for the coefficient of reflection of sound, we have

$$\rho = \frac{(m^{\frac{1}{2}} - n^{\frac{1}{2}})^2}{(m^{\frac{1}{2}} + n^{\frac{1}{2}})^2}.$$

The coefficient of absorption of sound, α, is the fraction of sound not reflected, or

$$\alpha = 1 - \rho = 1 - \frac{(m^{\frac{1}{2}} - n^{\frac{1}{2}})^2}{(m^{\frac{1}{2}} + n^{\frac{1}{2}})^2} = \frac{4}{m^{\frac{1}{2}}/n^{\frac{1}{2}} + n^{\frac{1}{2}}/m^{\frac{1}{2}} + 2}.$$

To find the coefficient of absorption, α, of a material, means must be provided (I.) for isolating a train of sound waves having a single period or pitch and a constant amplitude, (II.) for causing this train of waves to be reflected upon the surface whose absorption is desired, and (III.) for measuring the maximum and minimum intensities, *m* and *n*, of the resultant stationary wave.

METHOD OF PROCEDURE.

I. A tone of uniform intensity was produced by supplying an organ pipe with air from a pneumatic tank. This tank consisted of two sheet-metal cylinders closed at one end, the smaller of which was about 9 inches in diameter and 18 inches high and was placed, open end downward, into the larger which was half full of water. Air was drawn off by means of a faucet on top of the smaller tank and conducted to the organ pipe through ¼-inch tubing. The pressure of the air was regulated by adjusting a stop against which a rod soldered to the valve of the faucet would strike when the faucet was open the desired amount. The inner tank was weighed down by about 25 pounds of iron, thus making the pressure uniform for almost the entire air capacity.

To obtain a simple tone sound was passed through what might be called a tone screen which absorbed all the overtones leaving nothing but the fundamental. This tone screen is based upon Quincke's modification of Herschel's interference tubes described by Rayleigh.[1]

If *CD*, Fig. 3, is tuned to the pitch of sound waves traveling from *A* to *B*, and the opening at *C* is as large as the section of the tube *AB*, no sound will reach *B*—it is completely absorbed by the tube *CD*.

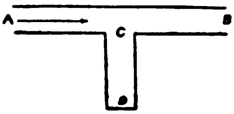

Fig. 3.

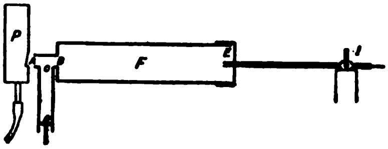

Fig. 4.

The truth of this was tested by taking a wooden flue, *F* (Fig. 4), of square cross-section 9 centimeters on a side and 115 centimeters long, placing a cap over end, *E*, through which projected a ½-inch glass tube from a sound-measuring instrument, *I*, and placing the interference tube or tone screen at end *B*. The tube *AB* was an inch hole bored in a block of wood 6 inches thick, and tube *CD* was a one-inch glass tube, the end *D* being a cork piston which allowed tuning of the tube. When the tube *CD* was removed, sound from the stopped organ pipe, *P*, passed through tube *AB* into the flue, *F*, and the measuring instrument indicated a large deflection. When the tube *CD* was in place and tuned to the organ pipe, the deflection of the measuring instrument was zero. (The tube *CD* was tuned to the fundamental of the organ pipe and hence also to its retinue of overtones, thus all of the sound of the organ pipe was absorbed.) When the tube was placed slightly out of tune with the organ pipe, a small deflection was obtained, and the deflection became larger as the dissonance was increased.

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[1] Lord Rayleigh, Theory of Sound, Vol. II., p. 210.

To isolate the fundamental tone of the organ pipe in the flue, *F*, four tubes similar to *CD*, tuned one to each of the first four overtones of the organ pipe, were placed around the passage *AB*. Since any overtones above the fourth for the organ pipe used were very weak if present at all, this constituted a very efficient tone screen. The tone in the flue was found to be simple by finding the sound intensity for each centimeter throughout the length of the flue and plotting a curve of intensity against distance. The curve was that of a simple tone.

A tone of uniform intensity having been obtained from an organ pipe, and its fundamental isolated in the flue, *F*, we must now ascertain whether or not the amplitude of the wave in the flue is constant throughout the length of the flue, as it is in Figs. 1 and 2. To this end, the first requisite is a flue of uniform cross-section to prevent the wave-front from spreading out and thus diminishing in amplitude. But if the flue lining absorbs the wave, the effect will be the same as a widening flue—the wave-front will spread out and both the progressive and reflected waves will diminish in amplitude as they advance.

Any detrimental presence of this lining absorption may be found by observing the maximum intensities all along the flue; they should be practically equal, otherwise the lining of the flue is absorbing sound.

Following are some readings made with a wooden flue and with the flue lined with felt (Fig. 5).

Lining absorption occurs in both cases, but a marked diminution from *B* toward *E* is seen in the case of the felt. A smooth, painted wood lining shows practically uniform maxima.

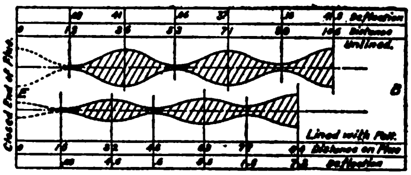


Fig. 5.

In connection with flue lining, the table of observations indicates that the wave-length shortens as the lining absorption increases. This means a decrease in the velocity of sound with increase of absorption. That the velocity of sound in pipes is not a function of the properties of the gaseous medium only but also of the absorption of the lining of the pipe may be simply shown by placing a strip of carpet along one side of a middle *C* organ pipe and sounding the pipe. Upon sounding without the carpet the pitch is seen to rise nearly a semitone.

To bring out more clearly that sound absorption plays a part in changing the velocity of sound in a pipe, and that the phenomenon is not due entirely to the elastic properties of the walls of the pipe, the following experiments were made:

One side of an organ pipe was replaced by a removable trough, *AB* (Fig. 6), stopped at the ends and about an inch deep. The pipe was sounded with this trough in place and the tone identified by means of a cylindrical resonator held to the ear. Between the trough and pipe were placed successively a smooth sheet of cardboard and a heavy fibrous sheet like blotting paper, and the resulting pitches of the pipe were identified; then the trough was filled with hair felt covered successively with the materials above mentioned, and the resulting pitches of the pipe identified; the trough was then filled with a block of wood and the pitch of the pipe identified. The result is given in the following table (Fig. 7). (The order designated by the crosses from the top downward gives the order that the materials were used with the pipe from the inside outward.)

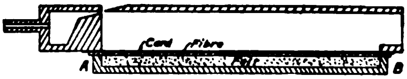
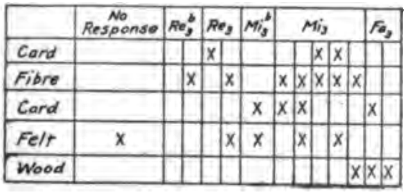


Fig. 6.



	No Response	Re^b_3		Re_3		Mi^b_3	Mi_3					Fa_3	
Card				X					X	X			
Fibre			X		X		X	X	X	X	X		
Card						X	X	X				X	
Felt	X				X	X		X		X			
Wood											X	X	X

Fig. 7.

When the felt, which is high in sound-absorbing quality and low in elasticity, is used alone, no tone could be produced. The absorbing power of the wall of the pipe decreases as we progress toward the right in the table, but it is seen that the elasticity of the surface exposed to the sound waves, and that of the under layers, has no regular change as we pass through this series. Take the tone mi_3, for instance: the elasticity of the wall consisting of fiber on wood is not the same as that of fiber on card over empty trough, and that of the latter is not the same as that of fiber on card on felt. For all of these combinations, however, the tone (and hence the velocity of sound) is the same.

An obvious relation between the elasticity and the sound-absorbing quality of a material is that, in general, as the former increases the latter decreases, but these phenomena lead to the conclusion that, while elasticity in the walls of a pipe may have some influence, direct or indirect, upon the velocity of sound in the air column, the velocity certainly decreases with increase of the sound-absorbing power of the walls of the pipe.

The influence on the velocity of sound in pipes due to a change in radius, elasticity and strength of wall, as well as the effect of compressibility and the temperature of the vibrating gas column, has been observed by Helmholtz, Kundt, Stokes, Schneebeli, Seebeck, Kirchhoff, Rayleigh, Korteweg, Dörsing, and others.[1] Korteweg's formula[2] for the velocity of sound in pipes,

$$c = c' \sqrt{1 + \frac{2}{CE} \cdot \frac{1}{e(1 - \frac{5}{8}e)}},$$

where c and c' are the velocities in free air and in a pipe, respectively, C is the compressibility of the fluid, E is the modulus of elasticity of the material of the walls of the pipe, and e is d/r, where d is the strength of the wall and r the radius of the pipe, gives a relation for the velocity of sound in the pipe to the radius.

This relation is shown by the following curve (Fig. 8), taking C equal to 10×10^{-7}, E equal to 10×10^{10} and d equal to 2.5.

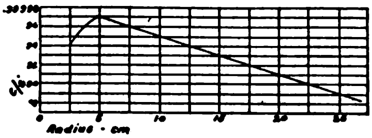


Fig. 8.

Except for tubes of very small diameter, this formula gives a decrease in velocity for an increase of radius. An increase in the radius of an organ pipe causes a lowering in the pitch of the pipe; also, from the experiment given above, an increase in the sound-absorbing power of the walls of a pipe causes a lowering of the pitch of the pipe, therefore, increasing the absorbing power of the pipe acts in the same way as increasing the radius of the pipe.

T. Boehm, in his book, "The Flute and Flute Playing" (translated by D. C. Miller), speaks[3] of the "flattening influence of the cork, mouth hole and tone holes." This flattening is undoubtedly an effect of the sound-absorbing power of the holes, or of that which covers them in playing.

II. If the flue, F (Fig. 4), were infinitely long, there would then be present in it a train of progressive sine waves, as shown in Fig. 1. Everywhere in the flue the sound would have the same intensity; there would be no reflected wave and, in the formula, m and n would be equal and α would be unity. Thus all sound is absorbed by an infinitely long flue.

If a surface (S, Fig. 2) be placed at the end, E, of the flue, F (Fig. 4), which reflects part of the sound, then the intensity throughout the flue would no longer be uniform but would consist of maximum and minimum regions, as shown in Fig. 2. If the intensities, m and n, can be measured, then the coefficient of absorption, α, may be computed by means of the formula.

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[1] Auerbach, Handbuch der Physik, Akustik, 1909, A. Winkelmann, pp. 539, 554; Theory of Sound, Rayleigh, Vol. II., pp. 29, 59, 317, 326.

[2] Auerbach, Handbuch der Physik, Winkelmann, p. 539.

[3] T. Boehm, "The Flute and Flute Playing," p. 18.

In using the flue in this way, the end where the absorbing material is placed must be closed air-tight with a cap in order not to have any "open end pipe" effect on the wave in the flue. If absorbing material has the inherent property of affecting sound waves as if the end of the flue were partially open (thus sending back waves with phase shifted one half wave-length), this interference would constitute absorption to the extent that it existed, and the material would behave to sound in this way wherever it was—whether it was stopping the end of a flue or decorating the wall of a room.

Any other "open end pipe" effect of the flue must be stopped. If the flue is a metallic cylinder, 4 or 5 inches in diameter, all crevices at the end, *E* (Fig. 9), may be done away with by means of the construction shown—a shrunk-on collar, *s*, over the finished surface of which the metallic cap, *c*, slides on and off. The absorbing material, *S*, is placed at the end of the flue, backed by any material, *G*, such as wood, that it is desired to use.

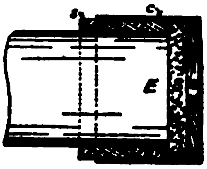

Fig. 9.

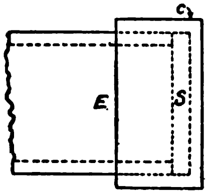

Fig. 10.

The flue used in the experimental work was made of wood of the dimensions already given. Its end, *E* (Fig. 10), was provided with a wooden cap, *c*, which served to hold the material, *S*, snugly against the flue and to close the end as nearly air-tight as possible.

III. In the search for means for measuring the intensity of sound tests were made of everything of any promise, and telephone receivers and transmitters,[1] strong and weak field galvanometers, molybdenite and silicon rectifiers, barretters[2] and microradiometers[3] all figured. The Rayleigh disc[4] was finally adopted as the most reliable and sensitive sound measuring instrument.

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[1] Prof. G. W. Pierce, Proc. Am. Acad., Vol. XLIII., 13, p. 377, 1908.

[2] Prof. A. E. Kennelly, Trans. Internat. Elect. Cong. St. Louis, 1904, Vol. III., pp. 415–437, 1905; Bela Gati, Engr., 105, p. 24, Jan. 3, 1908.

[3] Prof. F. R. Watson, Phys. Rev., 28, p. 385, 1909.

[4] Lord Rayleigh, Phil. Mag., Vol. XIV., p. 186, 1882.

The disc used was made of mica, 1 cm. in radius, suspended on a quartz fiber about 10 cm. long, a small mirror being fixed to the top of it like the mirror of a D'Arsonval galvanometer, but when the disc was turned through an angle of 45°, the mirror faced the front. It hung in a little wooden box with a glass front and two one-inch glass tubes led into opposite sides of the box so that, virtually, the disc was suspended near the center of a one-inch glass tube. This tube was stopped at both ends with corks, and was of such a length as to be in resonance with the sound employed. A one-half-inch glass tube about three feet long (the length adjusted to resonance with the pitch employed) pierced one of the corks and served to deliver the sound energy to the disc. A sound at the end of the long tube causes the air in the tube to vibrate, and an antinode, or region of greatest velocity of air particles, is formed where the disc hangs. As is well known, the disc tends to set itself at right angles to the direction of motion of the air stream, and turns through an angle which is a measure of the intensity of the sound at the end of the long tube.

The equation of the torque acting upon the suspended disc, as worked out by W. König,[1] is

$$M = 4/3\rho r^3 v^2 \sin 2\theta,$$

where M is the moment of the couple due to the stream of density ρ, flowing with a velocity v, and r is the radius of the disc whose normal makes an angle θ with the direction of the undisturbed stream. In the case of the sound vibrations the velocity v would be alternating and the air particles would move with simple harmonic motion, thus the energy due to the vibrations would be proportional to the mean square velocity. W. Zernov has shown[2] that König's equation holds for sound vibrations in free air, the v^2 being proportional to the intensity of the sound and equal to the mean square velocity of the air particles.

For use in measuring sound intensity, the Rayleigh disc is suspended in a resonance tube. It has been shown by Stewart and Stiles[3] that the intensity of sound in a resonance tube is proportional to the intensity of the exciting sound in the free air at the mouth of the tube. The following simple experiment also brings out this fact: A disc was hung near the mouth of a tube and a source of sound (an organ pipe) placed near the end of the tube (Fig. 11). A stop at d made the tube a resonator for the sound and deflections were made for several different distances of the organ pipe from the tube. The stop was then moved to d' thus throwing the tube out of resonance. The sound vibrations which affected the disc were then not due to resonance but were of the character of reverberation in a room and the disc responded as in free air. Deflections were again taken for the same distances of the organ pipe from the end of the tube. Following is the result — showing the same law to hold in both cases:

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[1] W. König, Wied. Ann., XLIII., p. 51, 1891.

[2] W. Zernov, Ann. der Phys., XXVI., p. 79, 1908.

[3] Stewart and Stiles, PHYS. REV., April, 1913, p. 309.

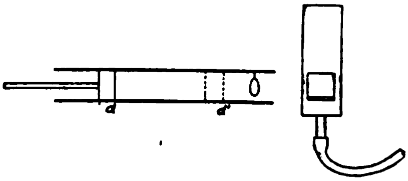

Fig. 11.

Case of Reverberation:

Organ Pipe Distance.	Deflection.
1 cm.	20.1
2 cm.	10.2
3 cm.	6.0

Case of Resonance:

Organ Pipe Distance.	Deflection.
1 cm.	36.0
2 cm.	18.4
3 cm.	10.8

The similarity in the behavior of the disc in the two cases is clearly shown by the similarity in the shape of the curves (Fig. 12).

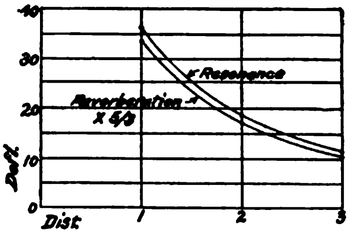

Fig. 12.

Thus the intensity of sound in a resonance tube is proportional to the intensity of the sound in free air at the mouth of the tube, and the deflections of a disc in a resonance tube are a measure of the intensity of the sound at the mouth of the tube.

With König's equation as a basis, the calibration of the disc for sound intensity may be worked out as follows:

When responding to sound, the disc turns through an angle which we will represent by ϕ. Since the apparatus was so constructed that $\theta = 45^\circ$ when there is no sound, then $\phi = 45^\circ - \theta$, and $2\phi = 90^\circ - 2\theta$. When the return torque of the suspending fiber is balanced by the couple acting on the disc due to sound vibrations, then

$$L\phi = M = kv^2 \sin 2\theta,$$

where L is the moment of torsion of the suspending fiber, and $k = 4/3\rho r^3$. (ρ, the density of the air, is a constant at an antinode of sound vibration.)

$$\cos 2\phi = \cos (90^\circ - 2\theta) = \sin 2\theta,$$

therefore

$$L\phi = kv^2 \cos 2\phi = qi \cos 2\phi,$$

where i (the intensity of the sound) is proportional to v^2, q being equal to k times the proportionality factor.

Then

$$i = \frac{L\phi}{q \cos 2\phi} = \frac{b2\phi}{\cos 2\phi},$$

where

$$b = \frac{L}{2q}.$$

Since the deflection, δ, on the scale is equal to $s \cdot \tan 2\phi$, where s is the distance of the mirror from the scale, then $2\phi = \tan^{-1} \delta/s$, and

$$i = \frac{b \cdot \tan^{-1} \delta/s}{\cos (\tan^{-1} \delta/s)} = \frac{b \cdot \tan^{-1} \delta/s}{s/(\delta^2 + s^2)^{\frac{1}{2}}}$$

$$= \frac{b(\delta^2 + s^2)^{\frac{1}{2}} \tan^{-1} \delta/s}{s} = h(\delta^2 + s^2)^{\frac{1}{2}} \tan^{-1} \delta/s,$$

where $h = b/s$.

For small deflections, δ^2 may be neglected in comparison with s^2, and the angle and its tangent may be considered equal, then the intensity of sound is proportional to the deflection of the disc, or

$$i = k\delta.$$

The error involved in using this approximate formula may be brought out by the following example:

Let the distance from mirror to scale, s, be 100 cm. and two deflections be $\delta_1 = 40$ cm. and $\delta_2 = 0.87$ cm.

Using the exact formula for computing relative sound intensity:

$$\frac{i_1}{i_2} = \frac{h \cdot 107.71 \cdot 21.8\pi/180}{h \cdot 100.004 \cdot \pi/360} = 46.96.$$

Using the approximate formula involves merely a comparison of the deflections:

$$\frac{i_1}{i_2} = \frac{40}{.87} = 45.84.$$

Thus the percentage error is $\dfrac{46.96 - 45.84}{46.96} \times 100$ or 2.2 per cent.—the approximate formula giving the smaller value for the louder sound.

The error involved in using the approximate formula for the computation of the coefficient of absorption, α, may be shown by using these results in the formula for α already derived:

For the correct ratio of sound intensities, $m = 46.96$, and $n = 1$; then

$$\alpha_0 = \frac{4}{m^{\frac{1}{2}}/n^{\frac{1}{2}} + n^{\frac{1}{2}}/m^{\frac{1}{2}} + 2} = \frac{4}{6.8527 + 0.1459 + 2} = \frac{4}{8.9986} = 0.4445.$$

For the approximate ratio of sound intensities, $m = 45.84$, and $n = 1$; then

$$\alpha_1 = \frac{4}{6.7702 + 0.1447 + 2} = \frac{4}{8.9179} = 0.4485.$$

The percentage error for the coefficient of absorption is

$$\frac{0.4485 - 0.4445}{0.4445} \times 100 = 0.9 \text{ per cent.}$$

As the ratio of sound intensities approaches unity, the percentage error decreases, therefore, for the computation of the coefficient of absorption, the approximate formula for relative sound intensity is close enough for material of high absorbing power but should not be used when the absorbing power is less than 0.20.

In agreement with the above calibration of the disc deduced from theoretical considerations, the result of the following experiment may be cited.

The disc was suspended in a resonance tube an inch in diameter and ¾-wave-length (about 30 cm.) long, closed at both ends except for four small glass tubes of one-eighth-inch bore lying across one end, each tube pierced with a little hole which opened into the resonance tube (Fig. 13). The tubes were mounted in a wooden cap which fitted nicely over the end of the resonance tube, and the whole arrangement constituted an adaptation of Quincke's interference tube. A sound passing through one or all of the four little tubes would be swallowed up by the resonance tube, if its pitch is that to which the latter is tuned. One end of each of these four tubes was fitted into the wooden cap closing end, *E*, of the wooden flue already described which served as a horn to catch the sound from an organ pipe placed at the end, *B*, and four little wooden rods were made of such a size as to slip into the glass tubes and stop all sound from coming into them.

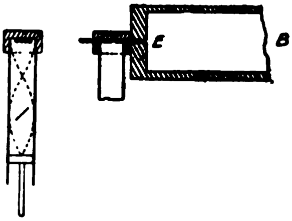

Fig. 13.

With one rod removed, the organ pipe was sounded and a deflection of the disc was noted. The resonance tube in which the disc hung had absorbed all of the sound which was passing through one little tube, and the disc felt the impulse of the sound vibration. The same was done with two tubes open, then three and then all four. The following is a sample of the deflections received:

Number of Tubes.	Deflection.
1	.12
2	.46
3	.98
4	1.96

The deflections are seen to run about in the following proportion: 1 : 4 : 9 : 16. Variations may be due to slight differences of bore in the tubes. The sound in the first tube produced a certain amplitude in the resonance tube; the sound in two tubes gave twice as great an impulse or produced twice the amplitude in the resonance tube, etc. All of the sound delivered to the resonance tube was very weak and could produce no great crowding of air particles, and so the amplitudes were able easily to be superimposed one upon another without loss of motion, and since the intensity of sound varies as the square of the amplitude, it would vary, also, in this case, as the square of the number of tubes delivering sound to the resonance tube. The resulting deflections very nicely confirm this, and since the deflections were all small they would come within the approximation made above which gave the final calibration formula, $i = k\delta$, deduced from König's law of the Rayleigh disc. Thus, for the Rayleigh disc, it is theoretically and experimentally established that, for small deflections, the intensity of sound varies as the deflection; for large deflections, the intensity may be computed from the more extended formula,

$$i = h(\delta^2 + s^2)^{\frac{1}{2}} \tan^{-1} \delta/s.$$

The calibration of the Rayleigh disc provides the necessary means for measuring the ratio of the maximum and minimum sound intensities in the sound flue (Fig. 4) and makes possible the calculation of the coefficient of absorption of sound by the use of the formula:

$$\alpha = \frac{4}{m^{\frac{1}{2}}/n^{\frac{1}{2}} + n^{\frac{1}{2}}/m^{\frac{1}{2}} + 2}.$$

When the Rayleigh disc is used to measure sound intensity the range of pitch is limited by the fact that the disc must lie in an antinode, and density variation of the air must be absent. For very short waves the disc would swing out of the region of constant density and thus complicate the calculation of sound intensity. For very high pitches, therefore, very small discs must be used. For a disc one millimeter in diameter there would be no great error when used with a wave two centimeters long, which would correspond to a frequency of about 16,500 vibrations per second, or a pitch of about C_9—six octaves above middle C (C_3—256 vibs./sec.). An octave and a half above this would take us to the upper limit of audibility, showing that the apparatus is applicable to any probable range of pitch.

The different parts of the apparatus used for making observations for sound absorption have already been described. The parts were assembled as shown in Fig. 14. The flue, *F*, moved along a graduated track, *T*. The one-half-inch glass tube, *IG*, from the suspended disc passed through the tone screen at *B* and projected into the flue. The intensity of sound at the end, *G*, of this tube causes the air in the tube to vibrate and this in turn produces a deflection of the disc.

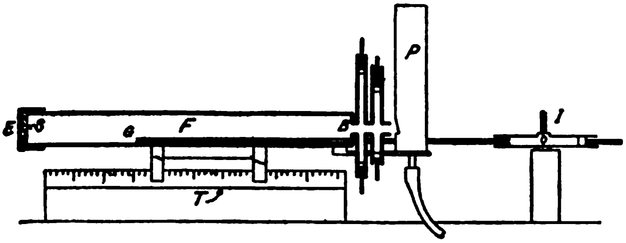

Fig. 14.

In taking observations, the flue, *F*, with the organ pipe, *P*, attached to it was moved along the track, *T*, in steps one centimeter long. Observations for intensity were made at each step, and at the region of maximum and minimum intensities for shorter steps, and thus the maximum and minimum intensities, m and n of the formula, were found. Applying these values in the formula, the coefficient of absorption of sound for the material, *S*, closing the end, *E*, of the flue, *F*, was calculated as already shown by an example.

Following is the coefficient of absorption of a few materials computed by using the approximate formula:

Material.	m	n	α
Smyrna Rug	6.55	.04	.26
Brussels Carpet	7.30	.03	.23
Hair felt (1-inch thick)	24.70	.78	.51
Ceilinite (½-inch thick)	57.50	.22	.25
Asbestos roll fire felt (⅛-inch thick)	54.50	.30	.26
Compressed cork (1½-inch thick)	27.00	.25	.32

The last four materials were kindly furnished by the Johns-Manville Co. of New York. The values of the absorbing power given here for the first three materials check fairly well with values obtained by the reverberation method.

The absorbing power of material is increased by increasing the space between it and the wall behind it. This may be explained by considering sound absorption as a retardation of the motion of the vibrating air particles; hence, by placing the absorbing material out a little from the wall (where the air is at rest) it becomes more effective in retarding motion and thus more efficient as a sound absorber. Following are the coefficients for compressed cork taken for several different distances between it and the board behind it:

Compressed Cork.

Distance from Board.	m	n	α
2 mm.	25.00	.25	.34
5 mm.	25.50	.34	.38
10 mm.	18.30	.46	.47
20 mm.	13.70	.74	.61

The relation is also shown by the curve (Fig. 15):

An important application of the flue to auditorium acoustics is the following: Sabine has found[1] that the reverberation of a room varies for different parts of the musical scale. To correct the acoustics of a room, therefore, absorbing material must be so applied as to make the reverberation for each tone normal. Since the absorbing power of a material varies with its distance from the wall, and this distance varies for the maximum absorption of each tone, it is possible to so graduate the distance of the material from the wall as to make the reverberation of the room for each tone of the entire musical scale normal. The flue makes the determination of the absorbing power of materials for variation of tone and distance from wall a simple matter.

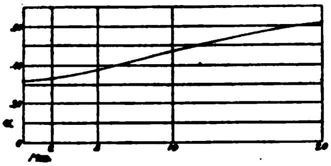

Fig. 15.

The flue method of finding the value of a material as a sound absorber eliminates the effect of the interference system of a room on the absorbing power of the material. As shown by Sabine[1] a material of high absorbing power placed in a room where, due to interference, the intensity of sound, or sound pressure, is very small would have little effect on the sound in the room, but if placed in a region of large relative sound pressure it would diminish the sound perceptibly.

If the absorbing power of this material were obtained by the reverberation method in this room in the first position mentioned, it would be found to be relatively small, and in the second position, relatively large. If one of these is the correct absorbing power, the other is not, and the probability is that neither is correct.

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[1] Prof. W. C. Sabine, Arch. Quar. of Harvard Univ., March, 1912, p. 20.

Conversely, if the correct absorption of a material is found by means of the flue, and this material is used to reduce the reverberation of an auditorium, its value will depend somewhat upon its position in the room. Thus the true power of absorption of a material will be useful in connection with auditorium acoustics only when used with due precaution—and then it is of much value. It is useful also as an index to give the material a rating with relation to other sound absorbing materials.

The power of materials to absorb sound transmitted through them was found as follows:

The wooden flue already described (Fig. 4) was stopped at end, *E*, by a board one-half-inch thick, through the center of which passed a one-half-inch glass tube from the Rayleigh disc, *I* (Fig. 16). The tone screen was removed from end *B* of the flue, and a closely fitting tin box slipped into the end. The two opposite ends of this box, through which the sound must pass to enter the flue, were made of cheese cloth and their distance apart was adjustable.

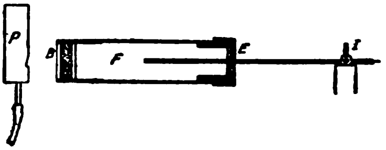

Fig. 16.

With this box in the end of the flue, *F*, and an organ pipe, *P*, placed immediately behind it, the first reading was made giving the intensity of the sound in the flue when end, *B*, was not closed with the material whose absorption was wanted. Then the cheese cloth ends of the tin box were adjusted for several different distances apart and for each one the box was filled with absorbing material and slipped into the end of the flue for a reading. Following are the readings made for water glass crystals loosely shaken down but not packed, the organ pipe sounding the note *si* (240 vibs./sec.):

Thickness. cm.	Deflection. δ.	Fraction of Sound	
		Transmitted.	Absorbed.
0	44.20	1.000	0.000
2	24.90	.564	.436
4	15.50	.352	.648
6	11.50	.260	.740
10	5.50	.124	.876
16	1.10	.025	.975
20	.53	.012	.988

The intensity of sound varies as the deflection, $i = k\delta$. If I represents the sound intensity transmitted through zero thickness of the material, and i the intensity transmitted through thickness, t, then i/I is the fraction of sound transmitted through thickness, t, and $1 - i/I$ is the fraction absorbed by thickness, t. The following equation gives the relation, when t is small:

$$i/I = (1 - \beta)^t,$$

where β is the fraction of sound absorbed by unit thickness (1 cm.) of the material. This fraction is the insulation coefficient for sound for the material.

The insulation coefficient for three materials follows:

Material.	β
Water Glass Crystals	.211
Hair Felt	.226
Compressed Cork (1-inch thick)	.500

The curve between observed thickness and sound transmitted shows the experimental relation (Fig. 17):

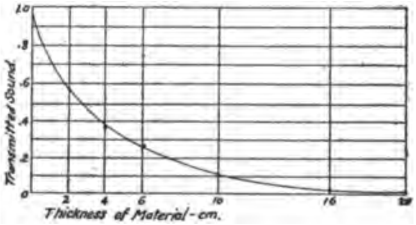

Fig. 17.

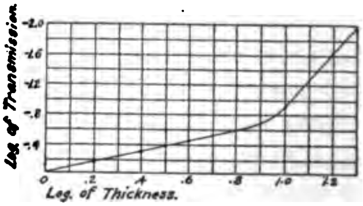

Fig. 18.

The curve between the logarithm of the fraction of sound transmitted and the logarithm of thickness shows that the logarithmic relation holds only when t is small, and that a distinct change occurs in the law of absorption in a certain region (Fig. 18):

The absorbing lining at the end, E (Fig. 16), of the flue makes internal reflection in the flue impossible. When sound strikes the outer surface of the material at the end, B, it is, in general, partially reflected, thus the amplitude of the wave which actually enters the material is not that of the incident wave. The coefficients given above express the relation between the incident and transmitted sound. Architecturally, this coefficient would probably be more useful than the coefficient based upon the sound which actually enters the material, since it is the intensity present in a room and incident upon a wall that one hears, and the wall is constructed to isolate this sound from adjoining rooms. Thus this is properly the insulation coefficient of a material for sound.

The intensity of sound which actually enters a material may be obtained by finding the coefficient of reflection, ρ, of the material when it is in place at the end, B, of the flue, F, and taking the product of this and the first deflection, δ_0, in the above table; δ_0 is proportional to the incident sound, therefore $\rho\delta_0$ is proportional to the reflected sound, and $\delta_0 - \rho\delta_0$ is proportional to the intensity of the sound entering the material. Simplifying, we have $\delta_0(1 - \rho) = \delta_0\alpha$, since $1 - \rho = \alpha$; therefore the intensity of the sound actually entering the material is proportional to the product of the deflection when no material covers the end, B, of the flue and the coefficient of absorption of the material when it is in place at the end of the flue with a column of air behind it. The fraction of sound transmitted when $\delta_0\alpha$ is used as a basis may properly be called the transmission coefficient of the material for sound, and it may be computed by using $\delta_0\alpha$ in place of δ_0 in the computations for $(1 - \beta)$.

Reflection from the outer surface of the material at the end, B, of the flue may be prevented by a covering of acoustically black material—loose felt. The sound transmitted by this covering may be found by making observations with it alone, and $\delta_0\alpha$ thus obtained experimentally.

The methods for finding the absorption of sound as outlined above may be applied in a number of ways; following is a partial list of suggestions:

(*a*) Determining the relation between the absorbing power of a material and its distance from the wall behind it.

(*b*) Determining the relation between the absorbing power of a material and pitch of sound.

(*c*) Determining the relation between the absorbing power of a material for transmitted sound and the thickness of the material.

(*d*) Determining the relation between the absorbing power of a material for transmitted sound and pitch of sound.

(*e*) Determining the relation between the absorbing power of a material and its composition or texture for a range of different pitches of sound.

(*f*) Determining the relation between the sound absorbing quality and elasticity of a material.

(*g*) Determining the absorbing power of materials by means of the effect of absorption upon the pitch of an organ pipe.

The Rayleigh disc may be used:

(*h*) For the detection of the presence of overtones in a sound by suspending it in a tube tuned to the pitch of the overtone.

(*i*) To bring psychological observations of ear accommodation up to a greater degree of completeness and accuracy.

Physical Laboratory,
Cornell University,
May 26, 1913.

ON TEMPERATURE AND SURFACE CONDITIONS WHICH AFFECT THE POSITIVE IONIZATION FROM HEATED PLATINUM.

BY CHARLES SHEARD AND D. A. WOODBURY.

TWO general views as to the nature of the positive ions from heated metals and metallic salts have been advanced in recent years. Richardson and Hulbirt[1] came to the conclusion that the positive ions from heated metals have an average value of m/H of 25.7. Some later determinations with platinum made by Richardson[2] gave an average value of m/H of 32.5. Professor Richardson has advanced the theory that the positive thermions are in large part charged atoms of sodium or potassium which are present as impurities in the form of salts. J. J. Thomson,[3] Horton,[4] Garrett,[5] W. Wilson[6] and Klemensiewicz[7] hold in general to the view that the carriers of the positive electricity from hot metals are for the most part molecules of gas absorbed by the metal. Recently another paper on this subject has appeared in which the writer, Dr. Horton,[8] is of the opinion "that the ionization from platinum (and from metals generally) is largely due to the emission of absorbed gases on heating."[9] A considerable portion of the proof in support of his conclusions rests upon the observed increase in the ionization effects after heating the wire, or salted anode, in a Bunsen flame.

The writers of this article will present the results of some experiments showing (1) that there are at least two sources of ionization present as impurities in platinum and that one of these becomes more operative and the other less so with continued heating due to the greater ease with which one of the sources is driven off by heating, and (2) that a wire, which has been so treated as to have become non-efficient in its emissive power, may be revivified so as to give greatly increased thermionic currents when its surface is cleaned.

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[1] Phil. Mag., p. 557, 1910.

[2] Phil. Mag., p. 989, 1910.

[3] Camb. Phil. Soc., Vol. XV., p. 64.

[4] Proc. Roy. Soc., Vol. 84, p. 433, 1910; Camb. Phil. Soc. Proc., Vol. XVI., pp. 89 and 318, 1911.

[5] Phil. Mag., Vol. 20, p. 582, 1910.

[6] Phil. Mag., Vol. 21, p. 634, 1911.

[7] Ann. der Phys., Vol. 36, p. 796, 1911.

[8] Proc. Roy. Soc., Vol. 88, p. 117, 1913.

[9] *L. c.*, p. 139.

The experiments to be described were made in dry air at atmospheric pressure. There are several reasons to be advanced in favor of this procedure rather than to carry on such experiments in a good vacuum. (1) The reproducibility of conditions when the apparatus has been opened, the wire treated, re-inserted and its ionization currents again investigated. Richardson and Sheard[1] found that the linear current-E.M.F. relation which holds initially for the positive currents from platinum (heated at temperatures such that no negative ions were present) at low pressures ultimately disappeared, giving place to saturation current conditions. The large additional currents were restored by allowing the apparatus to stand with air at atmospheric pressure in it. In the light of these experiments some of the results which have been published relative to the restoration of emissive power when a wire has been heated in a gas may be questioned, for the increased currents obtained after re-pumping may be due in part to this cause. (2) The elimination of effects due to contamination of the wire with mercury or phosphorous vapor; the first mentioned effect has been discussed recently by Horton.[2] (3) The ionization phenomena are of the same general nature whether performed at atmospheric pressure or in a vacuum as shown by H. A. Wilson,[3] O. W. Richardson[4] and W. Wilson.[5] The bulk of experimentation in this field has been carried out at pressures ranging from a small fraction of a millimeter to twenty or thirty millimeters. It is reasonable to assume, if the presence of a gas about the heated wire is an important factor in ionization effects, that the pressure of the gas will not affect the phenomena *qualitatively* but rather *quantitatively*.

Apparatus and Method of Experimentation.

The main chamber used in these investigations is sketched in the accompanying diagram, Fig. 1. A cylinder of brass, *A*, 11.5 cm. long and 6 cm. diameter, was closed at the ends with quarter-inch brass plates. Through the lower plate, *B*, two well insulated, heavy brass leads were passed. The platinum wire, *C*, 0.01 cm. diameter and about 3 cm. in length, was fastened tautly across the ends of the brass leads. The receiving electrode, *D*, consisted of a hollow cylinder of brass, 4 × 1 cm., attached to a micrometer screw passing through a threaded bushing of brass properly insulated from the remainder of the upper plate, *E*, by means of glass and sealing wax. The distance between the two electrodes could thus be changed at will; in the experiments to be described it was kept at 4 mm. The detecting electrode was kept cool by drawing air through a system of tubes, *NN*, passing inside the micrometer arrangement and attached at opposite sides of a brass partition within the electrode proper. With this form of apparatus it was possible to completely shield the insulation from the thermionic emission and also to avoid uncertainty as to the correct current values due to heating the receiving electrode. Such effects have been noted and investigated somewhat by Richardson.[1]

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[1] Phys. Rev., Series I., Vol. XXXIV., p. 391, 1912.

[2] *L. c.*, pp. 121 and 133.

[3] Phil. Trans., A, Vol. 197, p. 415, 1901.

[4] Phil. Trans., A, Vol. 207, 1908.

[5] *L. c.*, under (6).

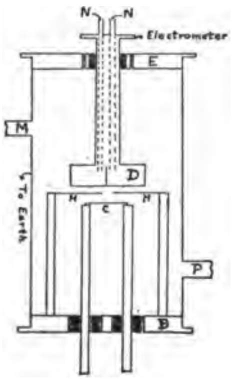

Fig. 1.

Some preliminary experiments showed that the length of wire made luminous increased considerably as the heating currents were augmented. The thermionic currents would in consequence be enhanced above true values as the temperatures increased. In order to avoid this source of error a plate, *H*, with a circular hole 1 cm. in diameter was placed 1.5 mm. from the platinum wire, the center of the opening in the plate being directly above the middle point of the wire. The plate *H* was fastened to metallic supports terminating in the plate *B*. This was earthed together with cylinder *A* and plate *E*.

Dry air or other gas was drawn into the main apparatus through calcium chloride towers connected at *M*, the needed suction being supplied by a water pump operating through *P*. Stopcocks were inserted in *M* and *P*; the plates *B* and *E* were sealed in with soft wax, the whole chamber being made air-tight. Ionization effects due to the presence of water vapor[2] were thus guarded against.

The platinum wire was heated electrically. The resistance of the wire was determined by the voltmeter-ammeter method. Two platinum leads (not shown in Fig. 1) were attached to the wire about 1 cm. from each end; the potential differences were read on an instrument graduated to 0.02 volt per division. It was possible to read the heating current to one one-thousandth of an ampere; constancy of current at any desired value was secured by a low-valued sliding resistance control. A linear relation existed between the calculated resistances and the currents; the projection of this line until it intercepted the resistance axis at the zero point gave a ready means of determining the absolute temperatures, the resistance at room temperature being that for which the value of the current was practically zero.

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[1] Phil. Trans., Vol. 207, p. 19.

[2] See W. Wilson, Phil. Mag., Vol. 21, 1911.

The thermionic currents were measured by a quadrant electrometer. Throughout this paper, unless specified to the contrary, one division per second represents 3.7×10^{-13} amperes. The wire was charged to any desired potential, while the receiving electrode was connected to one of the quadrants of the electrometer, the other being earthed. A subdivided microfarad condenser connected in parallel with the insulated quadrants was used for measuring currents beyond the range of the electrometer. Keys, electrometer, condenser and lead wires were properly screened in the usual manner.

The wire, before insertion in the apparatus, was cleaned in boiling dilute nitric acid and then washed in distilled water.

When the thermionic current had been reduced to the steady leak condition observations were made upon the relation between the current and the applied electromotive force. Saturation currents were obtained under an applied potential of 150–200 volts, the latter being used.

THE THERMIONIC EMISSION AS A FUNCTION OF THE TEMPERATURE.

Numerous experiments have shown the general applicability of Richardson's formula,

$$i = A\theta^{\frac{1}{2}}e^{-b/\theta},$$

to express the relation between the saturation thermionic currents and the absolute temperatures of the wire, provided the chemical nature of the source of ionization is unaffected by the temperature changes. This formula may be most conveniently used by testing the linearity of the relation obtained by plotting $\text{Log}_{10} I - \frac{1}{2} \text{Log}_{10} \theta$ against $1/\theta$. The curves given in Fig. 2 were plotted in this manner.[1] In Curve I the current readings were made in the following way: the heating current was adjusted to the desired value and, when constant, +200 volts was applied to the wire and the ionization current measured. The potential and the heating current were then cut off, the control resistance changed and the above procedure repeated. It was thus possible to obtain the maximum ionization current at any given temperature, previous experience having shown that there is no "fatigue" effect due to temperature alone. The values of the currents used in Curve I are given in Table I., column 2. A discontinuity is indicated at the points E, D_1. Repetition with a new wire gave a similar effect at about the same temperature (710–

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[1] The current values used in the plot are the number of divisions per second multiplied by 100.

730° C.). The accuracy of EE_1, shifted as it is from the line D_1B, is to be questioned, especially in view of the fact that at still higher temperatures than those indicated the initial thermionic currents decayed so rapidly, even under the most rapid method of experimenting, as to fall below the value of E_1 at 764° C. This is in part at least to be accounted for by the presence of the negative ionization which would make recombination a factor.[1]

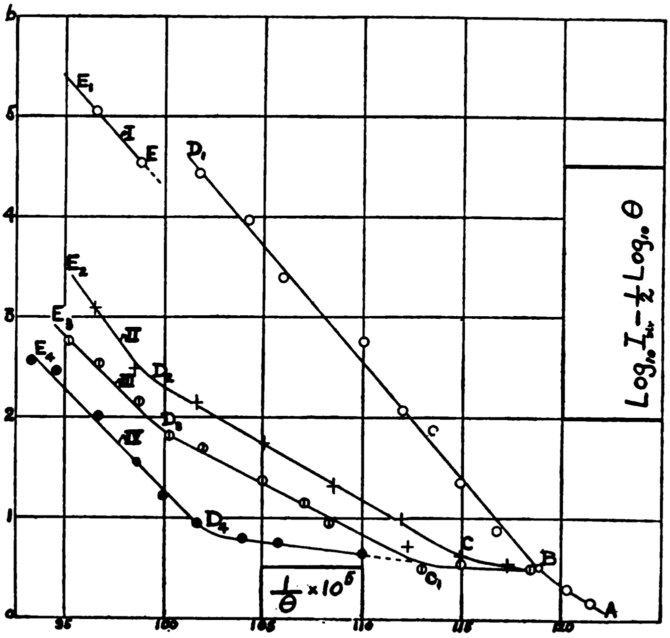

Fig. 2.

The values in Curve *II*, Fig. 2, were obtained as follows. The wire was heated at a given temperature and the decay of the ionization with time determined. The "slow decay" values of the currents were made use of in determining the relations given in *II*. A sample set of readings at 740° C. is inserted below.

Time (minutes)	0	1	2	3	6	8
Current	200	168	154	140	123	116

Time (minutes)	10	13	19	24	26	31
Current	110	105	85	78.5	78.5	79

Hence 79 div./sec. was taken as the value of the slow decay-with-time current. The order of heating, temperatures used, time of heating at each temperature and the slow decay current values are given in the appended table:

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[1] Under a potential of – 200 volts a negative current of 1 division per second, remaining constant in value during an hour's testing, was obtained at 705° C. The negative values were, however, always very small in comparison with the positive currents. After the positive emission had reached the condition indicated in Curve IV. at 764° C., a negative current of 1.5 divisions per second was obtained at that temperature.

Column.	1	2	3	4	5	6	7	8
Temperature, ° Abs.	845	869	893	923	953	983	1013	1040
Current, (div./sec.)	1.05	1.2	2.6	6.7	16.6	42.5	78.5	495
Time heated (min.)	30	35	35	28	28	28	30	18

Curve *III* was taken immediately after the highest temperature value of the current given in *II*. The readings were taken in the manner described in discussing Curve *I*, proceeding from lower to higher temperatures. Curve *IV* was obtained in an analogous manner after the wire had been left standing cold in the apparatus for eighty hours.

It appears, then, from an examination of these curves that there are two sources of ionization present as impurities in the wire. One of these becomes the predominant and permanent source of positive thermions at the higher temperatures as heating under potential is continued. The ionization from the second source is more easily driven off with heating and drops away with time more rapidly than that from the other substance capable of giving rise to positive ions and becomes in time practically inefficient as a producer of ions as shown in Curve *IV*, C_1D_4.

The tangent of the angles which the above lines (Fig. 2) make with the axis $1/\theta$ is a measure of the work done in setting free an ion. If it is legitimate to interpret all portions of these curves in this manner, then it is apparent, first of all, from the parallelism of EE_1, E_2D_2, E_3D_3 and E_4D_4 that the value of the work required to free a positive ion from one source of ionization remains constant under continued heating. The ratio of the tangents of the angles made by E_4D_4 and CD_2 with $1/\theta$ is equal to 0.57. The values of "*b*" calculated from the relation

$$b = \frac{\frac{1}{2}\log_e \theta - \log_e I}{1/\theta}$$

for the two portions C_1D_3 and D_3E_3 of Curve *III* are 2.4×10^4 and 4.5×10^4. Professor Richardson[1] has calculated the values of $\delta\phi$, the discontinuity of potential (in volts) between the metal and the surrounding space, as 2.45 for sodium and 4.1 for platinum. The ratio of these is 0.6. The writers of this paper venture the suggestion that the source of ionization operative at low temperatures is a sodium salt impurity and that the permanent source giving ionization from platinum at temperatures above 700° C. or thereabouts is a salt of another base, potassium, if we accept Richardson's recent work.

[1] Phil. Trans., Vol. 201, page 545.

The above experiments and the brief analysis made are in accord with Richardson's views. We quote the following from one of his recent papers:[1] "The gradual increase of *m* as the heating is continued is in agreement with the author's previous experiments on platinum.[2] It would seem to indicate that the source of positive ionization of lower atomic weight from platinum is more easily driven off by heating than that of higher atomic weight. The results are in agreement with the view that the ions of lower atomic weight are sodium atoms, but as the substance of higher atomic weight is less easily driven off by heat, it would appear that some impurity other than sodium or its salts has to be looked for."

CURRENT-TIME RELATIONS.

Additional support in favor of the above view is offered by the current-time relations plotted in Fig. 3. The wire was treated in a manner to be discussed later in this paper and its ability to produce ions under varying temperatures brought back approximately to the conditions indicated in Curve *II*, Fig. 2. Curve *1*, Fig. 3 (currents × 10), shows the steady valued current condition at 642° C., the readings being made after the wire had been previously used at 800° C. and 725° C. In Curve *2*, obtained at 725° C., there is an initial increase of the current to a maximum after two to three minutes before the decay sets in. Before taking the readings the heating current was adjusted until constant, the poten-

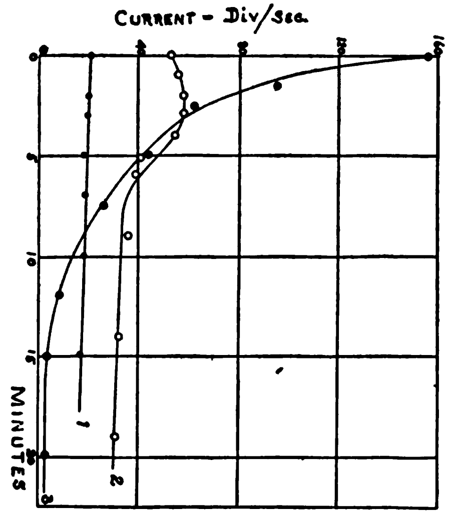

Fig. 3.

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[1] Phil. Mag., Dec., 1910, p. 993.

[2] Phil. Mag., Vol. 21, p. 759.

tial was then applied and the observations made. This method of operation it seems to us ensures the legitimacy of the results, for it eliminates errors due to slight resistance—and hence temperature-changes which often occur in the early stage of heating. Results similar in nature to those in Curve *2* were obtained when the current-time effects were investigated at temperatures considerably below those at which a wire had been previously treated until its steady current stage was reached. Horton has also noted the occasional occurrence of the initial increase of emission from reheated platinum.[1] The ionization currents, however, fell away from an initial maximum value when the wire was heated at 800° C. as shown in Curve *3* (currents × 100).

Current-time relations showing an initial increase were also found when obtaining the data used in Curve *II*, Fig. 2, at 596°, 620° and 643° C.

This initial rise of current during the first few minutes heating would be overshadowed completely if the second source of ionization, decaying with time in the manner shown in Curve *3*, were operative to any considerable extent. It is probable then that these two distinctive types of decay curves, indicating two sources of ionization, have not been definitely differentiated previously because (1) the current-time effects have not been investigated within the proper temperature regions after the wire

Table I.

Column 1. Temperatures in degrees absolute.
Column 2. Initial currents in divisions per second. See Curve *I*, Fig. 2.
Column 3. Currents after 30 hours' heating under potential at different temperatures.
Column 4. Currents after wire heated for 10 minutes in gas flame.
Column 5. Currents after heating electrically in hydrogen.
Column 6. Currents after wire brought back to "steady current condition."
Column 7. Currents after cleaning wires in nitric acid.

1	2	3	4	5	6	7
838	0.93	0.83	0.62	0.92	0.83	0.75
857	2.27	......	......	....	.....	....
868	6.65	2.00	6.75	3.6	0.80	0.74
881	23.4	......	......	....	.....	....
892	46.8	2.18	32.4	15.4	.....	....
910	183.0	1.88	61.5	64.7	1.16	13.3
934	835.0	1.82	78.0	110.0	1.18	46.2
958	2,900.0	2.00	92.5	423.5	1.18	819.5
982	8,850.0	2.94	......	4,785.5	.....	....
996	....	5.9	92.5	10,000.	4.15	2,035.5
1,012	10,400.	12.5	157.	12,210.	.....	....
1,036	38,400.	34.3	110.(?)	11,000.	5.5	3,666.
1,057	....	91.6	209.	16,940.	10.0	5,200.
1,072	....	110.0	363.	22,000.	17.0	10,000.(?)

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[1] Proc. Roy. Soc., Feb., 1913, p. 136.

has been treated for some time, and (2) the products of decomposition of one of the sources, the active and inactive, giving an ionization-time relation expressible by $e^{-\lambda_1 t} - e^{-\lambda_2 t}$, have rates of decay, λ_1 and λ_2, not widely different from each other; hence the initial increase of currents might be missed.

THE EFFECT OF A CHANGE IN THE SURFACE CONDITIONS OF THE WIRE UPON THE POSITIVE EMISSION.

Table I. contains a summary of the increased thermionic emission obtained when a wire, which has lost in a marked degree its power of producing ionization, was heated in the flame of a Bunsen burner (column 4), heated electrically in an atmosphere of hydrogen (column 5) or cleaned in hot dilute nitric acid (column 7). For the purpose of comparison the initial thermionic currents, as plotted in the ionization-temperature Curve *I*, Fig. 1, are given in column 2; the emission after thirty hours' treatment under potential and under various conditions of temperature in column 3. The lower plate *B* carrying the wire was removed from the apparatus after the readings recorded in column 3 had been made; the wire was heated intermittently for about ten minutes in the outer edge of the Bunsen burner flame, care being taken that the wire was not heated at a higher temperature than any previously used in these experiments. This was done by a visual observation of the luminous condition of the wire.[1] On re-inserting the wire and testing its emission it was found that the currents were considerably increased, especially at the lower temperatures. The effects were somewhat erratic, however, as an inspection of column 4 shows; the ratio of the values given in columns 4 and 3 showing a falling off from 40 to 1 at 934° Abs. to 3 to 1 at 1072° Abs. This general condition of increased currents disappeared very rapidly with continued heating and in thirty minutes time the currents had approximately the values given in column 3.

The wire was then heated electrically at 760° C. for five minutes in an atmosphere of dry hydrogen.[2] The current readings at various temperatures are recorded in column 5; the values of the currents being roughly one third to one half of the initial effects. The increased emission obtained after heating electrically in hydrogen did not decay to the low-valued emission condition, such as indicated in column 3, as quickly as when the wire was heated in the Bunsen flame.

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[1] The heating of the wire at temperatures in excess of any previously used in testing the ionization from a hot wire or salt must be carefully guarded against, for such a treatment of the wire will give greatly increased thermionic currents when again heated at any lower temperature which may be chosen. These last mentioned effects are being investigated further. It is possible that the increased emission observed by Horton after introducing a platinum wire or salted anode into a flame and heating it may be attributed to this cause and not wholly to the absorption of gas.

[2] Air became mixed with the hydrogen at this point causing an explosion. The wire was not disturbed from its supports and was used in further tests. In view of latter results it is probable that part of the increase of current obtained was due to the mechanical cleaning of the wire produced by the explosion.

Following the current readings given in column 6, the wire was washed for a minute or two in boiling dilute nitric acid, then cleansed in distilled water and when dry was replaced in the apparatus.[1] The thermionic currents following this treatment of the wire are contained in column 7. The relative magnitude of the currents before and after the cleaning in acid is as large and at several temperatures greater than the effects obtained by heating the wire in hydrogen.

The ionization from heated platinum is apparently a surface effect, and any change in the surface conditions of the wire, whether by heating in a gas or chemically cleaning, affects the subsequent ionization. That the use of a chemical reagent, which in itself has no effect upon platinum, should cause such changes in the ionization effects indicates the formation of a layer of practically non-ionizable material built up at or carried to the surface of the wire when heated for some time under potential. The residue of materials thus formed and not capable of producing ions would increase and become more operative with time and act as a blanket toward the "evaporation" of ions from the surface. It seems impossible to explain results such as those just presented on the theory that the chief source of the carriers of positive electricity from heated metals consists of absorbed gases. The function of a gas in restoring the power a wire has of producing ionization may be due to one or to all of several causes: first, a chemical change of such a nature as to render an inactive surface layer an efficient source of ionization; second, the removal of surface material by volatilization of new chemical compounds or combinations formed at high temperatures; third, in accord with some experiments by Reboul and de Bollemont,[2] the violent evaporation of absorbed gas may mechanically cleanse the surface. Some time ago Richardson[3] advanced the theory that "the effect of hydrogen is due to some changes it produces in the platinum surface"; he discusses this hypothesis at some length in the concluding paragraphs of the article referred to.

In the face of these experiments the writers are of the opinion that the weight of evidence is in favor of Richardson's view that the positive emission from heated platinum consists chiefly of charged atoms of sodium and potassium present as impurities.

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[1] The wire was not removed from its supports in any of these operations; otherwise criticism might justly be offered on the grounds of contamination in replacing the wire, etc.

[2] Comptes Rendus, 153, 1911, pp. 628–630.

[3] Phil. Trans., Vol. 207, 1908.

SUMMARY.

1. Two sources capable of producing thermions are present as impurities in platinum.

2. One source of ionization is more easily driven out by heating than the other.

3. After continued heating and when investigated within the proper temperature region, two distinct types of current-time curves are obtained; one showing a decay with time from an initial maximum, the other giving rise to a maximum after two or three minutes heating followed by the usual decay effects.

4. The thermionic emission from a wire which has lost its power of producing ions may be enhanced and made comparable with the initial effects by (*a*) heating in a Bunsen flame, (*b*) heating electrically in hydrogen, (*c*) cleaning the wire with acid.

5. The proposition is advanced that any change in the surface conditions of a wire or a salt will affect the subsequent ionization effects.

PHYSICAL LABORATORY,
OHIO STATE UNIVERSITY,
June, 1913.

THE REVERSIBLE ADIABATIC EXPANSION OF WATER.

BY J. R. ROEBUCK.

IF water be subjected to a change of pressure it is a matter of experiment that the temperature usually shifts slightly also. This temperature change depends upon the initial temperature, the initial pressure, and the pressure change. The work described here was undertaken on account of its bearing on the method for the determination of the mechanical equivalent of heat described in an earlier paper,[1] where a quantitative knowledge in a limited region of the relation between these variables was required. This relation has been studied both experimentally and theoretically by G. Tammann[2] who deduces the thermodynamic equation,

$$\left(\frac{dt}{dp}\right)_Q = \frac{T}{C_p}\left(\frac{dv}{dt}\right)_p,$$

where C_p is the specific heat of water at constant pressure and the subscript Q indicates adiabatic conditions. He integrates this equation arithmetically and obtains a set of curves which will aid in the discussion of this work if they are reproduced here, Fig. 1. The ordinates are temperature change from the initial temperature marked on each curve, and the final pressure is always the same, one atmosphere.

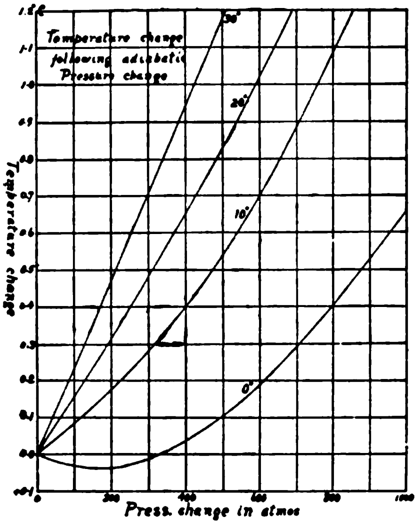

Fig. 1.

From these curves it is at once evident that by a suitable choice of temperature, pressure and pressure drop, the resulting change of temperature will be zero. It will also be evident that the pressure drop need not be always to one atmosphere, the condition in these curves, to have this condition filled. By the choice of one of these sets of conditions for the porous plug reading, the total temperature change occurring there (with a trifling correction) would be due to the work done on the water, that is, the only serious correction would be reduced to zero.

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[1] PHYS. REV., 2d Ser., 2, 79, 1913.

[2] Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen, p. 131.

Except with two points of difference the apparatus used for the work on the mechanical equivalent of heat was used here. The first difference was that the higher pressures frequently used required other apparatus for its measurement than the open tube mercury manometer. Some experience with spring gauges has shown them to be quite unreliable for close work. The trouble seems unfortunately to be connected with the elastic properties of materials and less seriously with the multiplying mechanism. To summarize, the reading depends somewhat on the time during which the pressure is on the gauge, increasing slightly with time. The reading is materially different when approached from a higher pressure from that obtained when approached from a lower pressure and this quite beside any lost motion or friction in the recording mechanism.

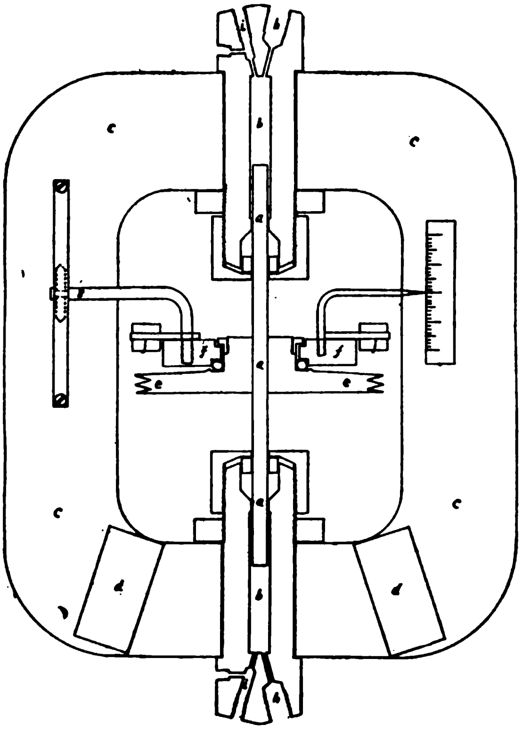

Fig. 2.

a, a, a, steel piston; *b, b*, cylinders; *c, c, c, c*, cast-iron yoke; *d, d*, lugs for legs; *e, e*, pulley; *f, f*, ring of ball bearing; *g*, arm for holding "*f*" from rotating; *h, h*, unions for pressure leads; *i, i*, relief cocks; *j, j*, ring for gimbals.

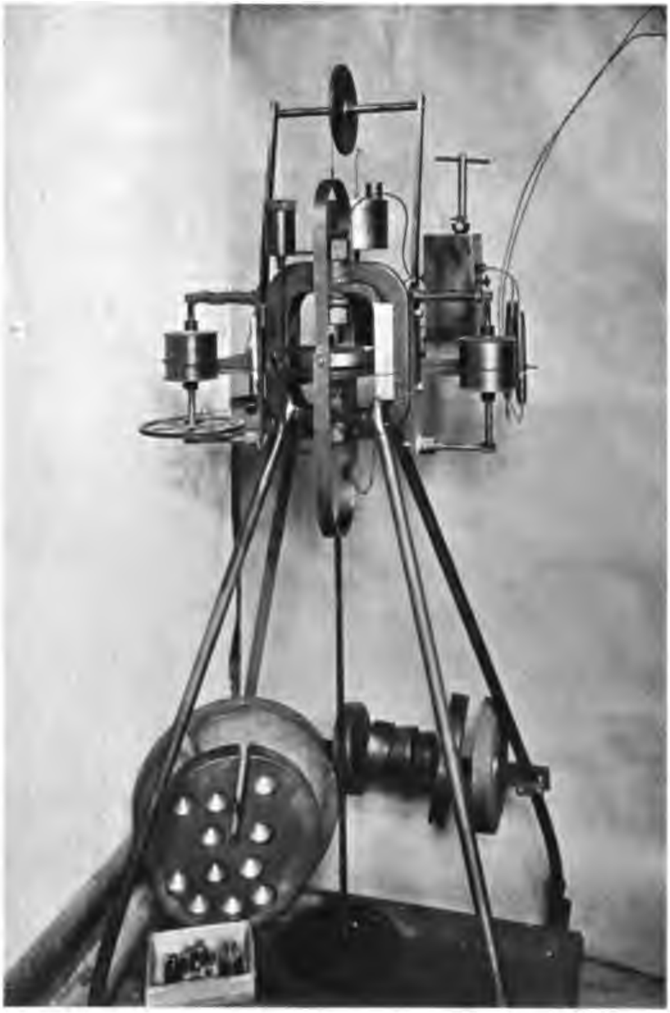

Fig. 3.

J. R. ROEBUCK.

The elasticity of the spring tube depends upon the temperature. Beside these grave faults, many even of the expensive gauges have serious errors due to the multiplying mechanism such as lost motion, friction and irregularity due to gear transmission. Their great advantages are their rapidity and ease of reading.

Experience with the rotating-piston pressure regulator had proved it to be so reliable, that a modified type of the engineer's dead-weight tester promised to give satisfactory results. Accordingly a differential manometer of this type was designed and its use in this and other projected work justifies a full description. It was built in the department shop by Mr. Foerst and no small part of its excellent performance was due to his accurate and careful work. A vertical section is shown in Fig. 2 and a photograph of the complete instrument in Fig. 3. Two cylinders (*b*) face each other on a common axis in a cast-iron frame (*c*) and are entered through leather packed stuffing boxes by a common piston (*a*) of glass-hard steel carefully ground and polished. At its center this piston carries a double grooved pulley (*e*) for rotating by round belts from two opposite cylinders under nearly equal tension. On the upper side of this grooved pulley (*e*) is a thrust ball-bearing carrying through gimbals (*f* and *j*) and a steel U, a vertical iron rod with a disk at the lower end for supporting the load of slotted iron weights. The arm (*g*) holds the gimbals from rotating while it allows vertical motion. All of these parts except the load are counterpoised by a weight hung over a pulley supported on hard-steel knife-edges. An iron cylinder attached to this counterpoise dips in mercury and serves to give the rotating cylinder a definite vertical equilibrium position. It is provided with a scale and was calibrated for displacement by small known weights. The cylinders were filled with paraffin oil and connected to the water system through U-tubes where the oil floated on the water. A block of steel carried the necessary relief cocks and valves. A single pressure was read by balancing the pressure admitted only to the lower cylinder, by a load of the iron weights; while a difference of pressure was read by admitting the higher pressure to the lower cylinder, the lower pressure to the upper cylinder, and balancing the difference by the load. The pistons were so nearly the same size that when in the symmetrical equilibrium position the same pressure up to 300 atmospheres applied simultaneously to the two pistons did not displace the zero beyond the experimental error of setting. The piston always returned from either direction in three to five minutes to within a mm. of the equilibrium position. A displacement of a mm. corresponded to 0.01 lb. load, or 0.2 lb. per sq. in. pressure. The slotted iron weights were standardized against the state standards at the state laboratory, for which courtesy my thanks are due to Mr. Dowling, in charge there. The diameter of the piston was measured with a micrometer calipers and over the part in use was exceedingly true. A simultaneous reading of a pressure on this instrument and on the open tube mercury manometer checked with this measurement of the diameter to 0.1 per cent. There was no leak past the leather packing and under these conditions it is difficult to see how a compression of the steel piston by the pressure used could influence the effective area of cross-section. Measurements of pressure due to the rotating-piston regulator could be duplicated to 0.1 per cent.

The second difference in the experimental arrangement was in the plug chamber. The plug was removed and the thermometer which had been inside the plug served for these readings. The other thermometer was removed to the bath and its place in the pressure system was taken by a device for stirring the water in the plug chamber immediately about the thermometer. A cylinder of very thin brass was placed around the thermometer and stirrer, so that the stirred water whose temperature changes were followed, was surrounded by a cylinder of water, not stirred, but subjected to the same pressure vibrations. The stirring of the inner chamber had to be limited to a very gentle movement once per minute or the effect of it showed at once on the thermometer.

In reading platinum resistance thermometers the best procedure is to use a continuous current so that the heating of the thermometer coils will be similar. In this work the addition of this energy to the water about the thermometer would have led to a marked rise of temperature when continued over the time for which the experiment lasted, so that it became necessary to make the bridge settings by momentary contacts of the Callendar key. This involves reading a small induction effect as resistance, though the bridge coils and thermometers were wound non-inductively, but since the resistance was varying within very narrow limits, a few thousandths of a degree at most, the induction effect would go out in the process of subtraction of the resistances to get the temperature change.

The experimental procedure was as follows: After the thermostat had been in steady operation for at least an hour, the stirrer was operated and the temperature read to 0.0001° C., once per minute, till the temperature became constant to about this amount, when the pressure was changed suddenly the predetermined amount by changing the load on the regulator, and the temperature again followed for about ten minutes. Usually in four to six minutes it was constant again, and in case the temperature change was large it often showed a drift at the end of the ten minutes. After an interval of thirty minutes to one hour this experiment was followed by a duplicate determination except that the pressure change had the opposite sign. The two readings usually checked to within 0.0003° C. but some showed large differences due probably to thermostat irregularities.

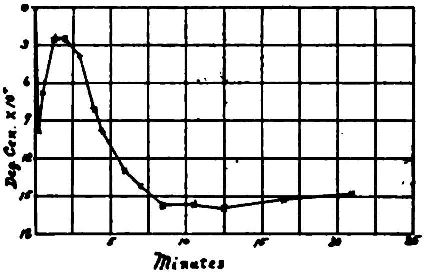

Fig. 4.

The temperature changes immediately following the pressure change are of some interest. Fig. 4 shows a typical curve, for a relief of pressure. Immediately following the pressure drop the thermometer records a sudden fall of temperature due probably to the work done by the thermometer case against the falling pressure. This is followed by a rapid return to the temperature of the water which may be above or below the initial temperature. In the case figured the temperature fell 0.0016° C.

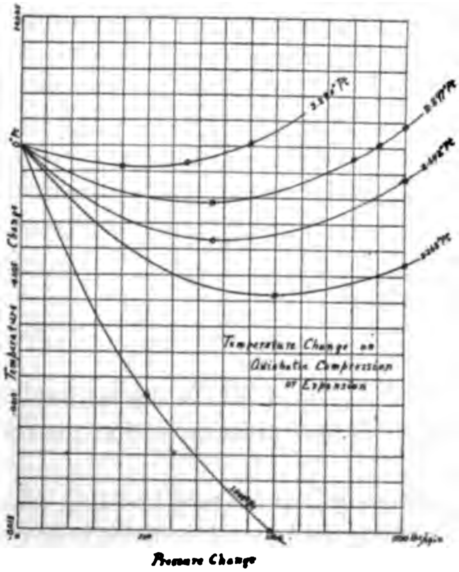

Fig. 5.

To explore the field generally a limited set of readings was taken between 0° and 4° C., with the lower pressure always one atmosphere, and the results are plotted in Fig. 5. This method of building up the curves does not give those which are the most useful. For each curve the initial temperature and final pressure are always the same, so that the curve does not represent exactly the path of the water during an expansion. For this either both initial or both final conditions should be alike for all points on a curve. But since the temperature change is so small and such a slight function of the initial temperature, the difference between the methods is immaterial. The curves are of the same form as Tammann's in Fig. 1. On attempting a numerical check it was soon apparent that the data on the coefficient of expansion at these temperatures were so uncertain as to make the calculations of little value. In the case of one reading at 26° C. the agreement was within the accuracy of reading from the original figure given by Tammann. Certain of these curves cut the axis for zero temperature change, which were the points of particular interest for this work. In general the temperature change is a function of the initial temperature, the initial pressure, and the pressure change. The particular value, $\Delta t = 0$, is consequently a function of all three variables. Fig. 6 gives the (p, t) relation of these points for the final pressure always one atmosphere. The curve cuts the temperature axis close to 3.96° C., in good agreement with the temperature of maximum density of water at atmospheric pressure, as was to be expected from Tammann's equation. The point at 3.59° C. was determined with especial care by varying the temperature at which the reading was made using the same initial and final pressures, and the readings are plotted in Fig. 7. This curve and the corresponding curve estimated from Fig. 5 give the temperature and pressure limits between which the mechanical equivalent had to be determined with this final pressure so that the correction should fall below 0.0001° C.

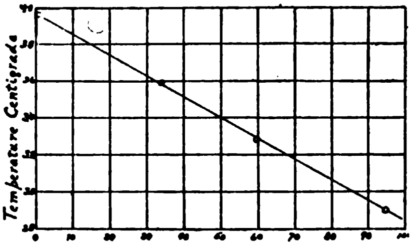

Fig. 6.

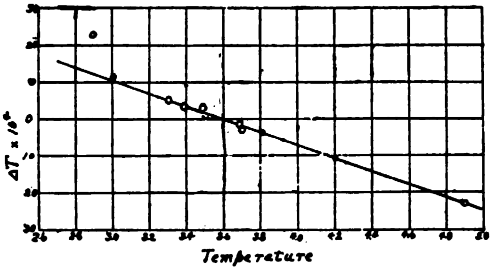

Fig. 7.

From Tammann's equation given above it is at once evident that when $(dt/dp)_q = 0$, then also $(dv/dt)_q = 0$, since the other quantities involved do not go to zero. That is to say, the maximum density conditions are also conditions where the adiabatic rate of change of temperature with change of pressure is zero. This offered another chance for experimental test of the theory and it was hoped might also prove to be a satisfactory method for the determination of the pressure-temperature relations of the maximum density. But the method proved exceedingly laborious and the results did not justify the labor required. The desired data called for the determination of $\Delta t/\Delta p$ at the limit $\Delta p = 0$. As a rule this is not possible and approximations have to suffice. Here it is possible, since the rate has positive, zero, and negative values. The procedure is to find a sufficient group of sets of conditions under each set of which $\Delta t = 0$; from which it is possible to interpolate for the set of conditions under which $\Delta p = 0$. The experiments deal with four variables and following the usual plan two are kept constant while the relation between the other two is being determined. The two, p and Δt, were chosen as being the most readily managed with the experimental set-up. A series of readings were made at constant temperature, of the temperature change due to a constant pressure drop from a series of initial pressures. If all four variables were chosen suitably, the curve obtained by plotting the experimental values of p and Δt cut the axis for p at which point $\Delta t = 0$. It was only necessary to plot the values as the readings progressed when from the trend of the curve p could be so chosen as to make Δt go through the zero value. This was repeated for other values of Δp but the same temperature, each curve giving a value of p and Δp at which for this temperature $\Delta t = 0$. Plotting of these values of p and Δp gave a curve cutting the p axis where $\Delta p = 0$, or at least by indicating the trend of the curve enabled the experiments to be so chosen as to make the curve cut this axis. For this cutting point then $\Delta p = 0$, also $\Delta t = 0$, so that $(dt/dp)_q = 0$, and the values of p and t therefore describe maximum density conditions. The whole process had then to be repeated for other constant temperatures, each repetition giving a new point on the maximum density pressure-temperature curve. A large number of readings were required to fix one of these points. The determination in duplicate of four to six points required a day's work. The data as reported could be improved by a larger number of readings, but the results did not promise to be as reliable as those by direct measurement of volume. None of the actual data is reported but only the final curve, Fig. 8. The points fall around Amagat's curve for the maximum density and hence may be taken as supporting Tammann's equation.

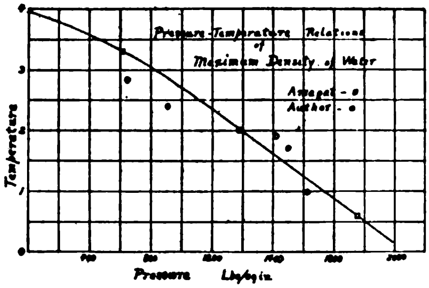

Fig. 8.

The principal contents of this paper are:

1. Description of an accurate rotating-piston differential manometer.
2. The method and data for fixing the point at 3.59° C. for the method for the determination of the mechanical equivalent of heat.
3. Experimental test of Tammann's curves, both direct and indirect.
4. Describes, tests and rejects an indirect method for the determination of the (p, t) relations of the maximum density of water.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF WISCONSIN,
June, 1913.

A DETERMINATION OF e/m AND v BY THE MEASUREMENT OF A HELIX OF WEHNELT CATHODE RAYS.

By J. B. Nathanson.

IN 1904 A. Wehnelt[1] showed that the output of negative carriers of electricity emitted from incandescent Pt, could be enormously increased by coating the Pt with a layer of an alkaline earth metal oxide like CaO. Using this Pt as a cathode, Wehnelt determined e/m and v for the cathode beam issuing from the hot lime. The method employed was the utilization of the potential difference of discharge and the measurement of the diameter of the circle into which the rays were magnetically bent. Wehnelt obtained an average value of 1.48×10^7 for e/m, and for v values ranging from 0.16×10^9 to 1.07×10^9 cm. per second. J. Classen,[2] employing a photographic method for determining the diameter of the circle, obtained a value of 1.773×10^7 for e/m. C. T. Knipp,[3] using the method of electrostatic and magnetic deflections, obtained a value of 1.5×10^7 for e/m and 1.6×10^9 for v.

In the present investigation, the method employed was the utilization of the principle of both magnetic and electrostatic deflections. This avoids the assumption that all of the electric energy of the electric field is converted into kinetic energy of the moving particles. Sir J. J. Thomson[4] has shown that when a moving electron is projected into a uniform magnetic and a uniform electrostatic field, the lines of force of both fields being parallel, that the electron will describe a helical path, the helix being of increasing pitch.

The helical path in the case of the Wehnelt cathode rays was experimentally realized as follows. The rays were projected from a Wehnelt cathode in a direction perpendicular to the lines of force of a uniform magnetic field. The path assumed by the rays was a circle. Upon application of a uniform electrostatic field whose direction coincided with that of the lines of magnetic force, the circle was drawn out into the form of a helix.

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[1] Ann. d. Phys., 14, p. 425, 1904.

[2] Phys. Zeit., 9, No. 22, p. 762, 1908.

[3] Trans. A. I. E. E., p. 1883, 1912.

[4] Thomson's Cond. of Elec. through Gases, 2d ed., p. 112.

The circular path of the rays is given by the equation

$$Hev = \frac{mv^2}{r},$$

or

$$v = H\frac{e}{m}r, \tag{1}$$

where H = magnetic intensity, r = radius of the circle.

The negative particles composing the rays, when projected in a direction perpendicular to the electrostatic field of strength Z, will receive a uniform acceleration of Ze/m in the direction of the field, so that in time t the electrostatic deflection z will be

$$z = Z\frac{e}{m}\frac{t^2}{2}. \tag{2}$$

If n is the number of times an electron has passed around the helix in the time t, while experiencing the electrostatic deflection z, then v, the velocity of projection of an electron, is given by

$$v = \frac{2\pi r n}{t}. \tag{3}$$

Evidently the time taken by the electron to go once around the circle with the constant velocity of projection v, is equal to the time taken by the electron to pass once around on its helical path with a resultant velocity v_R. Hence

$$z = \frac{Ze}{m}\frac{2\pi^2 r^2 n^2}{v^2}. \tag{4}$$

Substituting the value of v from (1) into (4) and solving for e/m, we have,

$$\frac{e}{m} = \frac{Z}{H^2}\frac{2\pi^2 n^2}{z}. \tag{5}$$

It was found very early in the investigation that the beam of rays after having passed the first time around on its helical path, would suffer a deflection or distortion when repassing over the cathode, this deflection being due to like sign of both cathode and electrons. As a result of this deflection, the uniformity of increase of pitch was disturbed, and it was therefore deemed advisable to measure the electrostatic deflection for the first one half turn only. Accordingly equation (5) reduces to

$$\frac{e}{m} = \frac{Z}{H^2}\frac{\pi^2}{2z} = \frac{\pi^2 V}{2dH^2 z}, \tag{6}$$

where V = potential difference of electrostatic plates, d = distance between electrostatic plates.

Eliminating e/m from (1) and (4) and letting $n = 1/2$, we have for v,

$$v = \frac{\pi^2 Vr}{2dHz}. \tag{7}$$

Description of Apparatus.

The discharge chamber consisted of a jar J, lying on its side, 21 cm. in diameter and 18 cm. deep. The mouth of the jar was ground plane to receive a square piece of plate glass P. This was fitted on airtight by means of a mixture of equal parts of beeswax and resin. The plate glass window permitted accurate measurements to be taken on the helix without any accompanying optical distortion.

The electrostatic deflections were affected by two parallel Al plates, A and B, resting on an improvised glass support S. These plates were circular, being 15 cm. in diameter. The upper plate A was connected through a water resistance to the (+) pole of the battery, the lower plate B, being connected to the (−) pole. With this arrangement the circle could be drawn out into a helix in an upward direction away from the lower plate. The difference of potential between the plates was measured by a Kelvin multicellular voltmeter.

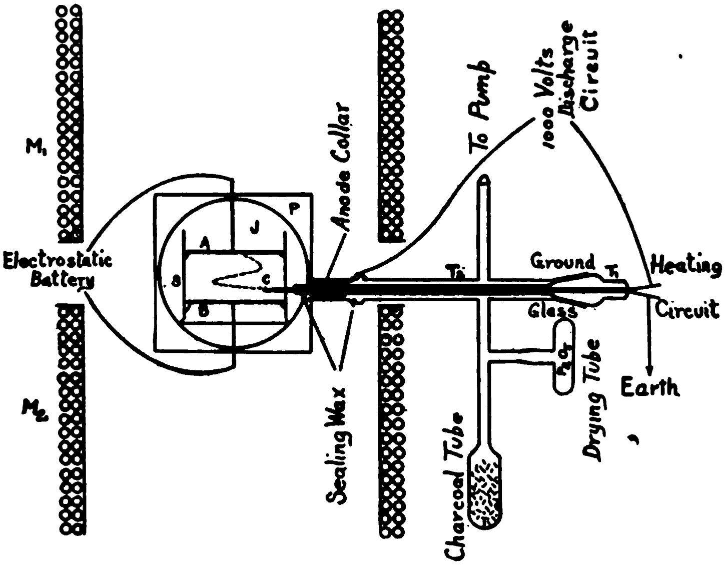

Fig. 1.

The discharge chamber with its electrostatic plates was surrounded by a uniform magnetic field, furnished by two large coils M_1 and M_2, each 41 cm. in diameter and 30 cm. high. By means of proper supports, they were separated from each other by a distance of 8.5 cm. This admitted the introduction of the Wehnelt cathode C into the discharge chamber, and at the same time allowed observations to be taken on the helix through the plate glass window.

A Grassot flux-meter was employed to determine the magnetic intensity H for any given value of the current I, through the coils. The discharge chamber was removed from within the coils, and the small test coil of the flux-meter was properly supported in the region occupied by the helix. Flux-meter readings were plotted against the values of I in amperes, giving a straight line curve through the origin. From the tangent of the curve, and the dimensions of the test coil, the following relation was found between H and I, where H is in gausses, and I is in amperes,

$$H = 5.7098I.$$

The maximum diameter of the cathode ray circle employed in this investigation was about 12 cm. To test the constancy of the magnetic field over this area, the small test coil was moved outwards from the axis of the magnetic coils, noting the flux-meter readings for various distances of the test coil from the axis, the current through the magnetic coils being kept constant. It was found that the flux-meter deflections were practically constant over a region of 16 cm. diameter. This therefore insured a constant field over the region traversed by the rays.

Since the beam of cathode rays issuing from the small lime speck on the Wehnelt cathode is so compact and well defined, the usual encumbrances of diaphragms, so necessary in the case of ordinary cold cathodes, were done away with, and the Wehnelt cathode was introduced right into the electrostatic field through a hole in the side of the discharge chamber. The manner of mounting the Pt strip on which the lime speck was deposited, was that employed recently by Knipp.[1] The ground glass joint permitted the rotation of the cathode about an axis perpendicular to the lines of magnetic force. The cathode beam could thus be oriented around till its path was perpendicular to the lines of magnetic force. This arrangement therefore admitted of easy adjustment for the obtaining of the beam in the form of a perfect circle.

The small lime surface was obtained by the placing of a minute particle of Bank of England sealing wax on the Pt strip and then electrically heating the strip slowly up to redness. The sealing wax was thereby changed into a small round white speck of lime whose diameter varied from 0.5 to 1 mm.

The discharge potential employed was 1,000 volts and was furnished by a large set of small storage cells. The cathode was grounded and connected to the (−) pole of the battery. The (+) pole was connected through a water resistance to the anode which was in the form of an Al collar on the inside of the tube T_2.

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[1] PHYS. REV., p. 58, January, 1912.

METHOD OF PROCEDURE.

The Wehnelt cathode rays are easily absorbed by any residual gas in the tube and hence are obtainable with distinctness only at a very high vacuum. The vacuum used was therefore the highest obtainable by means of a Gaede pump and charcoal cooled to liquid air temperature.

The cathode beam was started by closing the 1,000-volt discharge circuit, and then slowly heating the Pt cathode to redness. It usually took some time for the cathode beam to appear, the first appearance of the beam being in the form of a whitish flaky cloud. The temperature of the Pt was then slowly increased till the flaky cloud changed into a sharp beam which issued normally from the cathode. This beam was usually not perpendicular to the lines of magnetic force and hence when the magnetic field was applied the beam changed into a helix. By rotating the cathode in the ground glass joint, this helix was readily changed into a perfect circle which lay in a horizontal plane.

The telescope of the cathetometer was then sighted on the plane of the circle, the horizontal cross wire being placed on the horizontal edge of the circle at *a*, Fig. 2. Upon application of the electrostatic field, the circle was drawn out into a helix whose diameter was usually somewhat less than the diameter of the circle. The horizontal cross wire of the telescope was then sighted at *b* to obtain the electrostatic deflection for 1/2 turn, the difference in the cathetometer readings between *b* and *a* giving the amount of this deflection.

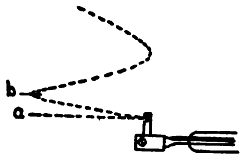

Fig. 2.

The diameter of the circle was measured by placing the leg of a square against the plate glass window, and moving the square along till the edge of the circle at one half turn was in line with the other leg of the square. The same was done for the other side of the circle at the cathode. The difference between the two positions gave the diameter to within 1 per cent., as close a measurement as could be warranted by the slight fuzziness of the boundary of the beam.

It was found that the lime would continually deteriorate and fall off from the hot Pt so that the beam would weaken and fade away with continual use. This necessitated the raising of the temperature of the Pt to bring the beam back again to distinctness. Thus during the course of an experiment, the temperature of the Pt was intermittently raised from red to white heat.

DISCUSSION.

The values of e/m vary from 1.27 to 2.07 × 10^7, giving an average value of 1.61 × 10^7. This agrees favorably with Wehnelt's value of 1.48 and Knipp's value of 1.5, but is less than Classen's value of 1.773 obtained by a photographic method. The values of v vary from 1.00 to 1.75 × 10^9 cm. per second, giving an average value of 1.39 × 10^9. We would of course expect v to vary with the different temperatures employed.

It might be instructive to check this value of v by another method. If V is the potential difference between anode and cathode, then we have from the equivalence of electrical and kinetic energy,

$$v = \sqrt{2\frac{e}{m}V}.$$

Supplying in this equation $V = 1{,}000$ volts, and $e/m = 1.61 \times 10^7$, v is found to be 1.79 × 10^9 cm. per second. This is somewhat higher, but of the same order, than the value of v experimentally obtained. However the actual difference of potential between anode and cathode had it been carefully examined, by means of a sounder, would have been found less than 1,000 volts.

TABLE I.

Distance between the electrostatic plates = 6.60 cm.

	Amperes, I.	Gausses, H.	Volts, V.	Cm., s.	Cm., $2r$.	$e/m \times 10^{-7}$.	$v \times 10^{-9}$.
1	3.30	18.84	81.3	1.01	10.1	1.71	1.62
2	3.99	22.78	81.2	0.85	7.7	1.39	1.21
3	3.33	19.01	79.5	1.08	10.0	.56	1.14
4	4.70	26.84	119.5	0.98	6.4	.27	1.09
5	3.20	18.27	80.0	1.10	10.0	.64	1.49
6	3.75	21.41	119.3	1.33	7.7	.46	1.20
7	3.43	19.58	79.5	0.99	9.3	.59	1.44
8	2.90	16.56	120.0	1.94	10.2	.70	1.43
9	3.62	20.67	83.0	1.01	8.1	1.44	1.20
10	2.90	16.56	120.0	1.72	10.3	1.91	1.63
11	3.61	20.61	126.0	1.30	8.7	1.71	1.53
12	3.35	19.13	43.0	0.43	8.9	2.07	1.75
13	4.20	23.98	120.0	1.05	7.2	1.49	1.29
				Mean...........		1.61	1.39

Returning to the values of e/m given in Table I., we notice that they vary somewhat among themselves. It seems that Wehnelt[1] had the same experience, for his table shows e/m to vary from 1.34 to 1.81 × 10^7.

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[1] Ann. d. Phys., 14, p. 425, 1904.

Since the method of this investigation is so different from Wehnelt's method, there seems to be no other conclusion than that the cause of the variation of e/m lies in the nature of the Wehnelt cathode itself. It was previously mentioned that the lime was continually disappearing from the hot Pt necessitating now and then the raising of the temperature of the Pt to obtain a sharper beam. Other recent work in this laboratory on the Wehnelt cathode shows quite conclusively that the activity of the hot lime, when supplied by Bank of England sealing wax, falls off rapidly with use—the current rising to successively lower and lower maxima each succeeding day when heated to the same temperature. It is evident, due to the sputtering of the hot lime cathode together with the probable complex character of the lime obtained from the sealing wax, that the source of the negative carriers of electricity is not a constant one. Slight variations in the heating current made correspondingly very large variations in the density of the cathode beam. This inconstancy must account in a large measure for the variation of e/m.

The disturbing effect of introducing the cathode between the electrostatic field plates was less than the error due to the variations just mentioned. This was shown to be the case by introducing the hot Pt strip carrying the lime up through a slot in the lower plate and adjusting so that the cathode beam, when bent into a circle by the strong magnetic field, just grazed the upper surface of this plate, the electrostatic field being zero.

In addition it might be said that, apart from all quantitative measurements, the helical method is most beautiful in its nature, and the apparatus serves very excellently as a demonstration piece for the magnetic and electrostatic deflection of cathode rays.

In conclusion I take this opportunity of expressing my thanks to Professor A. P. Carman for the facilities that were so kindly placed at my disposal, and to Dr. C. T. Knipp who made this work possible by his kind help and suggestions.

Laboratory of Physics,
University of Illinois,
June, 1913.

A PRACTICAL ELECTRICAL METHOD OF MEASURING THE DISTANCE BETWEEN PARALLEL CONDUCTING PLANES, WITH APPLICATION TO THE QUESTION OF THE EXISTENCE OF ELECTRON ATMOSPHERES.

BY F. C. BROWN.

IN the Philosophical Magazine for August, 1912, Professor R. W. Wood raises the interesting question of the existence of conducting atmospheres surrounding metallic surfaces. The necessity for this hypothesis arose from a number of experiments, in which electrical conduction took place between metallic surfaces, when they were separated between 20 and 30 wave-lengths of sodium light. The hypothesis appeals to the imagination but it is not easy to reconcile it with the well-known experiments by Earhart,[1] Hobbs,[2] Kinsley,[3] Almy,[4] Williams,[5] and others who found, by the use of interferometer methods, that there was good insulation when the conductors were much closer than the distances observed by Wood. Perhaps the argument may be urged against the interferometer methods that no allowance was made for a possible deformation of the metallic surfaces under the electrical stresses; nor have such methods as were used been infallible in detecting the absolute point of contact between the surfaces.

Moreover, Wood's experiments, considered alone, do not seem consistent with the electron atmosphere hypothesis, for such an atmosphere should extend out the same distance from the surface regardless of the insulating material between the surfaces, particularly so when the material is in discontinuous sheets. His results should not have shown a greater variation than the variation of his optical flat from that of a true plane.

I have tested an electrical method for measuring small distances in order to gain information which might help in explaining the above apparent discrepancies. I have found the method useful and the application interesting. The application can be most readily understood, after the method has been explained.

[1] Phil. Mag. (6), 1, p. 147, 1901.

[2] Phil. Mag. (6), 10, p. 617, 1905.

[3] Phil. Mag. (6), 9, p. 692, 1905.

[4] Phil. Mag. (6), 16, p. 456, 1908.

[5] PHYS. REV., 31, p. 212, 1910.

The electrical method of measuring the distance between two plane conductors is based on a measurement of the electrical capacity which the two planes possess by virtue of their nearness. For small distances such as I used the distortion of the lines of force at the edge of the planes was so small that no appreciable error arose therefrom, and the capacity of the connecting wires and the upper plane isolated was only from three to five units and could be corrected for or neglected. This method involves the elementary but fundamental and absolute formula,

$$C = S/4\pi d, \tag{1}$$

where C is the electrical capacity of the two neighboring surfaces of area S, and d is the distance between the electrical charges on opposite planes.

Now if it should be revealed that the distance between the opposite electrical charges is the same as the distance between the mechanical surfaces, then obviously it should be concluded that within the accuracy of measurement the electrical and mechanical surfaces are identical. In other words the identity would establish that an electron atmosphere does not extend beyond the mechanical surface. The question as to whether both negative and positive atmospheres exist need not be considered at this time.

The capacity of two parallel plates can be measured readily to a satisfactory degree of precision by the method of mixtures. I used a Dolazalek electrometer of 20 E.S.U. capacity for the comparison capacity and also for measuring the necessary potentials. The procedure was first to charge up one pair of quadrants to a potential V_1, represented by a deflection of the needle, D_1. The quantity of electricity on the needle was then allowed to distribute itself between the electrometer of capacity C_e, and the parallel plates of capacity C. The resulting potential, V_2, gave a deflection D_2. As usual the capacity of the parallel surfaces is,

$$C = C_e \frac{(D_1 - D_2)}{D_2}. \tag{2}$$

Substituting the value of the capacity in equation (2), the distance between the conducting surfaces is obtained in the form

$$d = S \cdot D_2 / 4\pi C_e (D_1 - D_2). \tag{3}$$

Because of the low capacities to be compared this method requires a high degree of insulation for all the parts. I have been very much surprised to find how easy it is to obtain almost perfect insulation when the neighboring plates are separated by only a few wave-lengths of light. The only precaution thus far found necessary is that the insulating material should be free from moisture and impurities. In general if material once dried is kept a few degrees above the atmospheric temperature, trouble due to moisture will be avoided. For very thin insulating material hours of heating may be required, so that it may insulate properly the conductors which it separates.

In these experiments I measured the distances between planes when the resistance was of the order of 10^{12} ohms, whereas Wood measured the distances when the conductivity could be measured by a galvanometer and a milli-ammeter. Naturally then I should have expected to work with planes separated farther than 20 or 30 wave-lengths, but I found in fact almost complete insulation at one or two wave-lengths, when the precautions mentioned were taken.

In 1908[1] I obtained insulating films which were only about 10^{-6} cm. thick. This is nearly a hundred times less than certain minimum insulating distances obtained by Wood. One of Wood's experiments indicated that a coating of oil did not interfere with the conductivity. So I tried first a film of turpentine. I evaporated a film of turpentine at high vacuum and allowed it to condense on a highly polished brass surface. After condensation I was able to bring up in vacuum a globule of mercury from below. The globule of mercury when earthed and brought up to the film altered the capacity of the electrometer system by the amount of the condenser formed. I was able to obtain by this method insulating distances of about 6×10^{-5} cm. As I was unable to measure the film thickness by a check method, it was not safe to conclude that the electron atmosphere did not extend into the turpentine.

The first experiments were made with conducting planes of hardened steel. They were made and polished by our instrument maker, Mr. M. H. Teeuwen, but the surfaces were not tested at the time optically for planeness, and the microscope showed them not to be free from scratches. However at the conclusion of all my experiments they were tested and found to vary from a plane by less than two wave-lengths. The area was about 1.8 sq. cm.

The two planes were separated by sulphur particles collected from an air suspension. Somewhat more than a thousand particles covered the surface of one of the plates, of which about 20 were larger than 0.007 cm. as seen by the microscope. When one of the plates was laid on the other there was complete insulation, *i. e.*, when the condenser was charged the potential did not vary noticeably in five minutes. The observations are shown in the following table.

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[1] Phil. Mag. (6), 18, p. 649.

These results indicate that the electrical method gives a shorter distance than the diameter of the sulphur particles, but it was not certain if the few largest sulphur particles might not crush or give or roll into the scratches under the pressure of the upper plate. Further it was not clear what action so many small particles would have on the dielectric constant of the intervening space.

Approximate potential across sulphur particles, volts....	4.34	3.4	1.8	0.6
Zero reading of electrometer, D_1....................	186	186	186	186
Reading of electrometer when charged, D_1.............	313, 329, 313	286, 289, 286	245, 247	205, 201, 201
Reading of electrometer when charges are mixed, D_2.....	225, 237, 234	225, 223, 226	205, 206	192, 193, 192
Capacity, E.S.U...........	36	32	40	28
Mean distance.............	0.0044 cm.			

Because the sulphur particles were not uniform in size and possibly not rigid, and because of the difficulty of getting rid of the moisture, I decided to try quartz fibers. A small fiber was broken into two parts and placed between the two surfaces. It was on a day in early May when the humidity was low, and the fibers were not previously heated, except in the oxygen flame when blown. Nevertheless the insulation was regarded as perfect. The following are the observations with these quartz threads separating.

Approximate potential between plates, volts..............................	2	0.9
D_1..................................	320, 319, 317	242, 245, 245, 244, 245
D_2..................................	209, 208, 208	195.5, 196, 195, 197, 195
Capacity.............................	100	103
Corrected capacity....................	97	100
Mean distance........................	.00151 cm.	

Now the size of the quartz fibers separating the planes as determined by the micrometer eyepiece on the microscope was

$$.00165 \pm .000086 \text{ cm.}$$

This difference by the two methods between the distances then varies by only about two wave-lengths. I found later in reading the size of fine fibers by the microscope, that it was much easier to err by obtaining values too large than too small. This experiment then leads to the conclusion that if there be a conducting atmosphere, it must not extend out more than two wave-lengths.

Obviously the conclusion just arrived at is inconsistent with Professor Wood's suggested interpretation of his experiment, in which he obtained a current of several milli-amperes when parallel planes were only five wave-lengths apart. I therefore thought it advisable to repeat the experiment using smaller quartz fibers, this time three in number. The sizes were:

First	.00052 cm.
Second	.00053
Third	.00059

And the mean probable distance of separation was therefore .00056 cm. The electrical method by the mean of five observations, with 0.3 volt across condenser, gave a separating distance of .00054 cm.

There are two conclusions that should be drawn from this experiment. First, there was almost perfect insulation when the two planes were separated by only ten wave-lengths, and, second, conducting atmospheres could not have extended as much as two wave-lengths outside the mechanical surface.

A further attempt to repeat the above experiments with yet finer quartz fibers met with failure owing to unsatisfactory insulation. I did not try heating the quartz fibers at this time because I feared that the steel surfaces might vary by ten wave-lengths. I observed that it was impossible by the electrical method to obtain insulation at distances less than those measured by the microscope. Unless some unknown factor is involved, this observation obviously leads to a third conclusion, which is that conduction at short distances arises from conducting material and not from an electron atmosphere of unvarying depth.

The question as to the imperfect insulation at less than 9 wave-lengths was still unanswered. Possibly the insulating properties of certain dielectrics break down when a certain minimum thinness is reached. It was thought that a constant minimum thinness for any given material would strengthen this view. Or perhaps as Wood suggested films of moisture about small particles might readily explain the imperfect insulation if not also the high conduction. We shall recur to this point in a succeeding paragraph. But the most opportune explanation, whose plausibility should be considered, was the possible irregularity of the steel surfaces.

The question of the planeness was answered in two ways. First, a glass plate with plane sides was moved over the surface of the plates and the character of the interference fringes noted. By this test the extreme variation of the surface was not as much as two wave-lengths.

Second, two optical flats on speculum metal were obtained, whose surfaces by optical test did not vary from a plane as much as one wave-length. With these my surprise was certainly great when I found imperfect insulation when the surfaces were separated by quartz fibers of 24 wave-lengths diameter. As my supply of quartz fibers, and also of oxygen was exhausted, I now turned to the use of mica flakes for insulation material. At first when a continuous sheet of mica of 25 wave-lengths separated the flats the insulation was imperfect. If charged to a potential of 4 volts, three fourths of the charge would leak off in 10 seconds, but by thoroughly heating the plates and the mica over an electric oven the insulation became quite perfect. This was more than a month after my experiments with the iron surfaces. and I now found it quite impossible to obtain good insulation without heating the plates and the insulator. Presumably the excess of humidity was the cause of the trouble.

In one instance the speculum surfaces were separated by three mica flakes of a total area of about 5 mm.^{2}. By the microscope one was about 14 wave-lengths, the second 12, in thickness. The third was not measured. When the electrometer was charged to + 5 volts and mixed with the speculum condenser the capacity was 310 cm., and when it was charged to − 5 volts the capacity was 315 cm. The total pressure on the upper plate was about 50 gm. From this capacity was subtracted 59 units as a correction for the added capacity due to the mica flakes and to the plate aside from its condenser action. The area of the plates was 1.84 cm.^{2}. The distance between the surfaces was therefore calculated to be .00060 cm. It seems safe to conclude from this experiment that the difference between the electrical and optical methods is not more than three wave-lengths.

It was observed that if the pressure on the plates was increased to 100 gm. the insulation became very poor. Sometimes the insulation would be restored by removal of the pressure and sometimes not. However increased pressure did not always alter or destroy the insulation.

Again three very thin mica flakes were selected. By direct reflection they all appeared a brilliant green, but when viewed by the light that struck at a very large angle of incidence some of them appeared orange colored. With these flakes between the flats the speculum plates slid over each other freely as if nothing was between, and likewise they resisted pulling apart. The electrical resistance between the plates was very low, although I did not measure it. Continued heating with the two plates together did not restore the insulation, although the mica had been heated for hours before the flakes were separated off the sheet mica.

Then the plates were separated and heated for two hours over an electric oven. The temperature of the plates was kept at about 215°. The mica flakes stuck tight to the plates during this procedure, although some of them did break in pieces. By this the insulation was made almost satisfactory, as may be seen from the following observations. It was necessary to determine the deflection from the first few swings of the needle. The period of the electrometer needle was about 10 sec.

	Pressure 90 gm.				30 gm.			
Zero	0	0	0	0	00	0	0	0
D_1	+33	+33	−43	−43	−82	−83	−80	−80
D_2	1	1.5	− 2	− 1.5	− 3.5	− 3.5	− 3.6	−4.0 after 10 sec.
								−3.2 after 20 sec.
Mean of D_2		1.5						−2.2 after 30 sec.

Mean		3.65
Corrected mean		4.45
Distance	.00031 cm.	.00043 cm.

Since heating the mica and plates to 215° had made the insulation so nearly satisfactory, it seemed wise to repeat this treatment. The plates were kept covered with japanese silk tissue to prevent dust particles from settling on them. After six hours the plates were removed while hot and tested at once. The insulation was not perfect but it was improved and at the same time the capacity was larger. At the beginning of the test the natural leak was such that the electrometer needle went from 3 div. to 1 div. in 50 sec. At the end of the observations the natural leak was from 2.7 to 1 in 20 seconds, from 1.0 to .5 in 30 sec., showing that the insulation deteriorated with time, possibly owing to the formation of a film of moisture as the plates cooled. The natural leak was corrected for in calculating the distance. The observations shown in table on page 321 were obtained before the insulation deteriorated seriously. I was not able by the microscopic method to determine the thickness of the mica flakes, further than to limit their probable size to less than five wave-lengths. This much also was determined by a micrometer screw gauge. Then interference fringes were formed by bringing two optical flats on glass into contact along one edge and allowing the opposite edges to be separated by the mica flake. The number of fringes between the point of contact and the mica obviously gives twice the thickness of the mica in wave-lengths. The great difficulty in this measurement was that sometimes considerable pressure had to be applied in order to bring the

Zero	0	0	0	0	0	0
D_1	32	32	32	−81	−81	−82
D_2, 10 sec.	.25	.5	.5	− 1.0	− 1.25	− 1.3
20 sec.				− .5	− 1.25	− 1.0
						Mean.
Zero	0	0	0	0	0	
D_1	−82	−82	+83	+83	−82	
D_2, 10 sec.	− 1.25	− 1.0	+ 1.0	+ .8	− 1.25	1.1±.14
20 sec.	− 1.0	− .85		+ .4	− 1.0	

Mean corrected	1.4
Capacity	1,170
Distance, cm.	.00013

plates into contact at one edge, much greater than was applied to the speculum metal plates. There was considerable irregularity in the pressure required to cause contact, and it may have been that, after heating, the speculum metal plates were separated only by the thickness of the mica. At any rate one of the mica flakes measured in this way had a thickness of two and a half wave-lengths, another one of two, and a third one of only one wave-length.

I observed after the second heating that the mica flakes on speculum surfaces showed the same deep green color that they exhibited when free. This rather indicates close contact between the mica and the speculum. Also the fact that long-continued heating permitted the electrical charges to come closer together, when separated by mica, indicates that heating either drives off something that conducts and separates, or alters the structure of the surfaces. If the mica flakes were in contact with the speculum, then there can be no conducting atmosphere of more than two wave-lengths of light, for this I regard as about the safe limit of accuracy of my experiments, but if on the other hand there exists a conducting atmosphere which is at the same time a mechanically separating medium, then it would not be safe to set such a low limit on the thickness of a possible electron atmosphere. The question will not be definitely settled until the distances are measured simultaneously by the two methods. We propose to do this by using very thin films of platinum deposited on plane glass surfaces. It is hoped thereby to finally decide to a fraction of a wave-length whether or not an electron atmosphere exists, and also to obtain information on the rôle played by insulating materials of small dimensions.

In as much as heating certain insulators such as mica and quartz restored their insulating properties, it is certain that the conduction obtained by Wood at such long distances was due to the presence of the insulating material, and it is presumed that films of moisture and conducting particles were responsible for it.

In conclusion it may be said that while the electrical method was satisfactory as here used, it can be more accurately adapted to the problem in hand by more suitably choosing the suspension for the electrometer needle and by using a larger capacity in parallel with the electrometer.

The State University of Iowa.

ON ELECTROMAGNETIC INDUCTION.

By S. J. Barnett.

1. In a recent article[1] on electromagnetic induction and relative motion published in this journal, and in a preliminary paper[2] published in the Physikalische Zeitschrift, I referred incidentally and briefly, and of necessity adversely, to some work on unipolar induction[3] by Mr. E. H. Kennard, who has now published three articles[4] in reply, the last in the May number of this journal. Although, in my opinion, Mr. Kennard's fallacies are quite apparent to anyone familiar with this part of electrical theory, it seemed advisable to make a reply[5] to the first of these articles on its appearance; and a final reply is now necessary.

2. In each of the three articles Mr. Kennard either states or implies that my chief criticism of his work is on account of his treatment of the dielectric on the moving line hypothesis. My chief criticism of Mr. Kennard's work has always been that even if his moving line theory were absolutely correct when applied to the ordinary case of unipolar induction in which the complete field-producing agent rotates, his sweeping conclusion from his experiments would be entirely without justification. For in his experiments the iron core of the electromagnet rotated alone while the magnetizing coil remained fixed like the condenser; yet his calculation of the effect to be expected on the moving line hypothesis assumes that on this hypothesis all the lines in his experiments would move with the iron. But it is quite impossible to say what fraction of the lines, on this hypothesis, would adhere to the iron and move, and what fraction would adhere to the coil and remain at rest. For the same reason, viz., that a part of the field-producing system was at rest, instead of all being in motion, the experiments are without value in connection with the matter of relativity.

3. In treating the problem of unipolar induction in a fixed dielectric

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[1] Physical Review, 35, 1912, p. 323.

[2] Phys. Zeit., 13, 1912, p. 803.

[3] Phil. Mag., 23, 1912, p. 937.

[4] Phys. Zeit., 13, 1912, p. 1155, and 14, 1913, p. 250; Physical Review (2), 1, 1913, p. 355.

[5] Phys. Zeit., 14, 1913, p. 251.

Poincaré,[1] Abraham, and myself have each assumed that throughout the field (points within the rotating magnet not being included) the electric density is proportional to the divergence of the *total* electric intensity. Mr. Kennard says that this was the assumption made by Hertz,[2] but that it is not always allowable on the theory of Lorentz. These statements are both true. But it is also true and well known that in fields such as that under discussion, in which the intensities are steady and the ether and matter at rest, *Lorentz's theory and Hertz's theory and Maxwell's theory are completely identical* so far as the total intensity, displacement, and density are concerned; and that in this case the assumption referred to is not only allowable but necessary. Mr. Kennard says that this assumption "may easily be shown to be incompatible with the moving line theory," and attempts to prove his assertion as follows: He writes the equation

$$\operatorname{div} f = \operatorname{div} (E + e) \tag{1}$$

in which E, e, and f are the field, motional, and total intensities, and applies the equation to a point in a dielectric of free ether at which the electric density, and therefore div f, according to Poincaré, Abraham, and myself, are zero. This gives

$$\operatorname{div} e = - \operatorname{div} E. \tag{2}$$

Mr. Kennard then *assumes, without justification*, that div $E = 0$. Then he calculates div e and finds that it does not vanish—a particular case of a well-known relation to which he has repeatedly called attention. Hence he concludes that (1) and (2) cannot be correct, and therefore that I and the others are wrong. The trouble, however, is only with the false assumption div $E = 0$.

4. To come to the next point, which I did not realize that my treatment could have left in obscurity, *I have certainly assumed that moving lines of induction act on the ether precisely as on a material dielectric.*[3]

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[1] Poincaré assigns to the dielectrics, magnet, and other conductors velocities which may vanish in particular cases. His treatment of the subject on Lorentz's theory is not correct for the case in which the velocities of the dielectrics differ from zero; and his conclusion that so far as experiment can show "the theory of Lorentz leads to the same results as that of Hertz" in the general case is erroneous. When the dielectrics move the two theories give quite different results; but on each theory the result is independent of the hypothesis adopted with reference to the seat of the electromotive force.

[2] Mr. Kennard's statement that Hertz "rejected the motional intensity" cannot be accepted.

[3] This is also an implicit assumption in the work of Poincaré and Abraham. For in the case under discussion the total intensity f differs from the field intensity E (whenever there is a difference) only by the motional intensity e. As another discussion of unipolar induction manifestly based on the same assumption should be mentioned that of S. Valentiner (Phys. Zeit., 6, 1905, p. 10), which, as far as it goes, is essentially identical with my own.

Mr. Kennard says that this is not consistent with current electrical theory as he knows it. It is nevertheless old and sound doctrine, universally accepted since the days of Maxwell.[1] It is involved in the fundamental relation between the electromotive force around a closed circuit in the ether at rest and the rate of change of magnetic flux through the circuit—a change produced, according to Maxwell, by the *motion* of the lines of induction across the circuit, since the lines of induction are closed curves—coupled with the relation between intensity and displacement. Among many obvious examples, one whose mere mention should be sufficient is the case in which the energy of a magnet set into motion is transformed into electromagnetic energy and transferred to an adjacent electric circuit in accordance with Poynting's theorem. As to Mr. Kennard's ideas on the diametrical opposition of ether to matter, etc., no remarks seem necessary.

5. The calculation of the charge on the condenser in my experiments to be expected on the moving line hypothesis when the field-producing agent rotates and the condenser remains fixed (Case II.) Mr. Kennard proceeds to make by *assuming* that the charge would be the same as when the condenser rotates and the field-producing agent remains at rest (Case I.). His reason for this appears to be the false assumption that the moving lines would have no effect on the ether. Had Mr. Kennard taken proper account of the ether, he would have obtained the charge *zero*, exactly as if the lines had been assumed to remain fixed. Because his calculation gave a charge independent of the magnitude of the dielectric cónstant, he stated in a previous paper, referring to my criticism that he had not taken proper account of the dielectric, that the trouble could not be with his treatment of the dielectric. But the neglected ether is an important part of the dielectric.

6. In his concluding paragraph Mr. Kennard says that he has elsewhere called attention to the fact that my conclusion as to relative motion rests in part on an inference.

Now it follows immediately and necessarily from the experiments of Faraday, Lorentz, Rayleigh and others on the motion of conductors in magnetic fields, together with the experiments of Blondlot, H. A. Wilson, and myself on the motion of insulators in magnetic fields, that if the condenser, whatever the magnitude of the constant of its dielectric, rotates while the agent producing the magnetic field remains fixed (Case I.), the condenser receives a charge equal to the product of the capacity as it would be with ether alone as dielectric by the rate at which the short-circuiting wire cuts across magnetic flux; and that if the material part of the dielectric is air, as in my own recent experiments, it is of no consequence whether the air moves with the conductors or not.

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[1] See, for example, Heaviside's Electromagnetic Theory, I., § 48; Lodge's Modern Views of Electricity, p. viii and §§ 114, 115; and S. Valentiner, *loc. cit.*

In the first of my original papers I referred only to the fact of the condenser's becoming charged; and in the second I referred, in addition, only to the "experiments of Faraday and others" as establishing the fact. Probably I should have gone into greater detail. This I have done in the Physikalische Zeitschrift, 14, 1913, p. 251; and in Science, January 17 and February 21, 1913.

The brief statement of fact, without reference to authority, in my first paper drew from Mr. Kennard the criticism to which he refers. He said that I had failed to give experimental proof of my statement. References to the experimental work having been given later, however, Mr. Kennard now objects to the experiments of Blondlot, Wilson, and myself on insulators on account of sliding contacts, stationary connecting wires, absence of a conducting screen, etc. These objections are entirely inconsequential and irrelevant and I shall not consider them further. No one will object to the repetition of any or all of these experiments, either modified or unmodified, by anyone who is sufficiently interested in them; but it is quite certain what the results will be.

7. In conclusion it seems desirable to consider briefly what happens on the theories of Hertz, Einstein, and Lorentz in each of the two principal experiments involved in the discussion of relative motion. As above, the case in which the condenser rotates will be referred to as Case I.; that in which the condenser remains at rest, as Case II.

On the theory of Hertz, the condenser is uncharged in Case I. and also in Case II.

On the theory of Einstein, the condenser is charged as indicated in § 6 in Case I., and charged in the same way in Case II.

On the theory of Lorentz, the condenser is charged as indicated in § 6 in Case I., and is uncharged in Case II.

Lorentz's theory is thus the only one which is consistent with both sets of experiments.

THE OHIO STATE UNIVERSITY,
June 7, 1913.

THE PHOTOELECTRIC PROPERTIES AND CONTACT RESISTANCES OF THIN CATHODE FILMS. II.[1]

By Otto Stuhlmann, Jr., and Karl T. Compton.

A second point of interest about Fig. 3 is that the curves are approximately logarithmic. It is known that the absorption of light also increases logarithmically as the thickness of the film increases. This would support the view that the number of emitted electrons is at least approximately proportional to the amount of light absorbed in the film.

Finally, attention should be called to the "humps" observed in two of the curves at *A* and *B*. Here the current increases rapidly, then decreases and again increases more slowly. This same phenomenon was consistently observed by Robinson.[2] For some reason this phenomenon was not present in curves 5 and 8. Apparently the normal course of the curve in this region would be that indicated by the dotted lines. The first departure below these dotted lines has been shown to be due to faulty contact. Several explanations of these maxima in the curves have been considered but we have not sufficient data to support any of them. We simply, therefore, call attention to this peculiarity without attempting to explain it.

Summary.

The most important results of this investigation are:

1. Thin platinum cathode films emit photo-electrons with maximum velocities at least approximately the same as those emitted by ordinary platinum. The intrinsic potential of these films is also the same, or very nearly the same, as that of ordinary platinum. If variations in these quantities occur, due to the as yet unknown properties of very thin films, they are certainly small.

2. The high photoelectric potentials which we observed, and doubtless those observed under similar conditions by other investigators, were due to the presence of soft wax or grease inside the sputtering apparatus.

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[1] Concluded from the September number.

[2] Loc. cit.

3. The saturation currents from thin sputtered films appear to be larger than those obtained from ordinary platinum. They increase approximately logarithmically with the thickness of the film and are therefore proportional to the amount of light absorbed by the film.

4. The method of making contact with the films has a great influence on the observed electrical properties of very thin films.

In conclusion we wish to thank the departments of physics of Princeton University and the University of Pennsylvania for the generosity with which they placed the facilities of their laboratories at our disposal. We especially wish to thank Professor O. W. Richardson for his suggestions and continued interest in our work.

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THE

PHYSICAL REVIEW.

THE VAPOR PRESSURE OF METALLIC TUNGSTEN.[1]

By Irving Langmuir.

The vapor pressure of metals has been the subject of many investigations in recent years.

Greenwood[2] has directly determined the boiling points of several metals at three or four different pressures. The method adopted was to heat the metal in a carbon or magnesia crucible in an electric furnace and to observe the temperature at which drops of metal were first thrown up from the molten surface. The metals studied were copper, tin, silver, lead, bismuth, antimony, magnesium, iron, chromium, manganese, and aluminum. The boiling points at atmospheric pressure ranged from 1120° C. for magnesium to 2450° for iron.

Recently von Wartenburg[3] has determined quantitatively the vapor pressures of lead, silver, and thallium by the dynamical method, that is, by passing an inert gas very slowly over the heated metal and measuring the concentration of the metal vapor in the gas.

The volatility of many metals has been qualitatively observed, but except in the case of the metals given above and such easily volatile metals as mercury, zinc, and the alkali and alkaline earth metals there are no quantitative determinations of the vapor pressures or boiling points known to the writer.

The volatility of the materials used for filaments of incandescent lamps is the principal factor determining the useful life of such lamps.

Experiments were therefore undertaken to determine the rate of evaporation of tungsten in vacuum at various temperatures up to the melting point.

The kinetic theory enables us to calculate the vapor pressure from this rate of evaporation, or at least to obtain a lower limit for the vapor pressure.

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[1] A preliminary statement of the results of this investigation has appeared in the Journal of the Amer. Chem. Soc., *35*, 931, 1913.

[2] Chem. News, *104*, 31–33, 42–45, 1912.

[3] Z. f. Electrochem., *19*, 482, 1913.

RELATION BETWEEN VAPOR PRESSURE AND RATE OF EVAPORATION IN A VACUUM.

Let us consider a surface of metal in equilibrium with its saturated vapor. According to the kinetic theory we look upon the equilibrium as a balance between the rate of evaporation and the rate of condensation. That is, we conceive of these two processes going on simultaneously at equal rates.

In the case of liquids or solids at temperatures near their boiling points or even at temperatures so low that their vapor pressures are in the neighborhood of one millimeter, we are accustomed to consider that there must always be equilibrium between the vapor and the liquid or solid at the surface between the two. For example, no matter how rapidly we may boil water we are probably justified in considering that the steam is saturated at the surface boundary between the water and the steam.

This, however, simply means that when we boil water as rapidly as we can, the net rate at which steam is produced is very small compared to the actual rate at which the water is evaporating into steam and the steam again condensing on the water.

At much lower temperatures, where the vapor pressure is of the order of magnitude of .001 mm. the rate of evaporation of a substance even in a practically perfect vacuum is very small. This is not due to the cooling of the substance by its own evaporation, but simply to the fact that the rate at which the molecules of vapor are formed is limited.

For example, we cannot make mercury freeze by placing it in a very high vacuum, although we know it has a perceptible vapor pressure even at its freezing point.

At temperatures so low that the vapor pressure of a substance does not exceed a millimeter, we may consider that the actual rate of evaporation of a substance is independent of the presence of vapor around it. That is, the rate of evaporation in a high vacuum is the same as the rate of evaporation in presence of saturated vapor. Similarly we may consider that the rate of condensation is determined only by the pressure of the vapor.

Now the rate at which the saturated vapor comes into contact with the metal may be readily calculated from the principles of the kinetic theory when the vapor pressure is known. Certainly the rate of condensation of the vapor cannot exceed the rate with which it comes into contact with the solid or liquid.

This calculation is similar to that of the effusion of gases through small openings.[1]

Let us consider a unit cube of the vapor one side of which is bounded by the metal. We will calculate the rate at which the vapor comes into contact with the metal. Half of the molecules in this unit volume are moving towards the metal, and the other half are moving away from it. If we let ρ be the density of the gas, then the mass of gas moving toward the metal is $\frac{1}{2}\rho$.

Let Ω be the average (arithmetical) velocity of the molecules. It can be readily shown that the average *component* of the velocity in any given direction is then $\frac{1}{2}\Omega$. Hence the average velocity with which the gas molecules in the mass $\frac{1}{2}\rho$ are *approaching* the metal is $\frac{1}{2}\Omega$. The mass of gas (m) which strikes against the unit surface of metal per second is therefore $\frac{1}{2}\rho \times \frac{1}{2}\Omega$, thus

$$m = \tfrac{1}{4}\rho\Omega. \tag{1}$$

The ordinary gas law $pV = RT$ may be written

$$\rho = \frac{pM}{RT}, \tag{2}$$

where p = pressure,
M = molecular weight,
T = absolute temperature (° Kelvin),
R = gas constant = 83.2×10^6 ergs per degree.

The average velocity (Ω) of the molecules is given by the relation

$$p = \frac{\pi}{8}\rho\Omega^2, \tag{3}$$

whence from (2)

$$\Omega = \sqrt{\frac{8RT}{\pi M}}. \tag{4}$$

Substituting (2) and (4) in (1) we get for the rate at which the vapor comes into contact with the metal

$$m = \sqrt{\frac{M}{2\pi RT}} \cdot p. \tag{5}$$ [2]

If we can assume that every atom of the vapor which strikes the metal condenses, then the equation (5) gives the desired relation between the vapor pressure and the rate of evaporation in vacuo. If, however, a certain proportion (r) of the atoms of the vapor is reflected from the surface then the vapor pressure will be greater than that calculated from (5) in the ratio $1 : (1 - r)$.

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[1] Cf. Meyer's Kinetic Theory of Gas, German edition, 1899, p. 82.

[2] This equation has been previously used by the author in calculating the velocity of reaction between oxygen and tungsten. Jour. Amer. Chem. Soc., 35, 106, 1912.

There are good reasons for believing that the reflection of vapor molecules from the surface takes place to a negligible degree only. Knudsen[1] has shown from measurements of the heat conductivity of gases at low pressures that the number of molecules of a gas which are reflected from a smooth surface (*i. e.*, do not reach thermal equilibrium with the surface) is as much as 70 per cent. in the case of hydrogen but very much less with gases of higher molecular weight. Knudsen gives the name accommodation coefficient to the quantity $1 - r$. He finds for example

Gas.	Surface.	Accommodation Coefficient.
H_2	Polished platinum	0.36
CO_2	Polished platinum	0.87
H_2	Platinized platinum	0.71
CO_2	Platinized platinum	0.98

Timiriazeff[2] finds the accommodation coefficient to have significance in determining the "slip" of gases in viscosity measurements at low pressure.

The accommodation coefficient for a vapor with such high molecular weight as that of tungsten would probably be nearly unity for any kind of surface. There is every reason to believe, moreover, that the accommodation coefficient would be particularly high in the case of a metal and its own saturated vapor. It is extremely probable therefore that equation (5) gives a very close approximation to the true vapor pressure.

Knudsen[3] has determined the vapor pressure of mercury at temperatures from 0° to 50° by a method involving the use of an equation similar to (5). He used a relatively large surface of mercury, however, and allowed the saturated vapor thus obtained to escape through a small opening into a space practically free from mercury vapor. From the rate of escape of the mercury he calculated the pressure of the vapor by an equation equivalent to (5). This method differs in principle from that employed for the present determination of the vapor pressure of tungsten only in having an opening through which the vapor diffuses instead of having the vapor simply diffuse out through the surface of the metal itself. Knudsen's method has the advantage that his results are practically unaffected by any possible reflection of the vapor molecules from the surface, but it has the disadvantage that is cannot be directly applied to determining the vapor pressures of such difficultly volatile substances as tungsten.

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[1] Ann. Phys., *34*, 593, 1911.

[2] Ann. Phys., *40*, 971, 1913.

[3] Ann. Physik., *29*, 179, 1909.

VARIATION OF THE RATE OF EVAPORATION WITH THE TEMPERATURE.

The relation between the vapor pressure of any substance and the temperature is given by the Clausius-Clapeyron formula.

$$\lambda = T\frac{dp}{dT}(v - v_0). \tag{6}$$

In the case of tungsten the volume of the metal is entirely negligible as compared to the volume of the vapor, so we may place $v_0 = 0$. If we consider λ to be the latent heat of evaporation per mol of tungsten (184 grams) then since $pv = RT$ we have

$$\frac{d\ln p}{dT} = \frac{\lambda}{RT^2}. \tag{7}$$

This result could have been obtained directly from Van't Hoff's equation.

In general λ is a function of the temperature such that

$$\frac{d\lambda}{dT} = C_v - C_s, \tag{8}$$

here C_v is the specific heat (per mol) of the vapor (at constant pressure), and C_s is the specific heat per mol of the solid metal.

We may safely consider tungsten vapor to be monatomic[1] and hence its specific heat at constant pressure is

$$C_v = 2.98 + R = 4.96 \text{ calories per gram atom.} \tag{9}$$

The atomic heat of solid tungsten is given as 6.3 by Gin (1908) and as 7.8 by Corbino.[2] The higher value is rather improbable, so that the best value would seem to be about

$$C_s = 6.8. \tag{10}$$

Substituting (9) and (10) in (8) and integrating we have:

$$\lambda = \lambda_0 - 1.8T. \tag{11}$$

This result substituted in (7) and integrated gives, after changing from natural to common logarithms:

$$\log p = A - \frac{0.218\lambda_0}{T} - 0.9 \log T, \tag{12}$$

where A is a constant of integration.

Taking the logarithm of equation (5) we obtain

$$\log m = \log p + \tfrac{1}{2} \log \frac{M}{2\pi R} - \tfrac{1}{2} \log T. \tag{13}$$

Combining this with (12):

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[1] Langmuir, Jour. Amer. Chem. Soc., *35*, 944, 1913.

[2] Phys. Zeitsch., *13*, 375, 1912.

$$\log m = A' - \frac{0.218\lambda_0}{T} - 1.4 \log T, \tag{14}$$

where

$$A' = A + \tfrac{1}{2} \log \frac{M}{2\pi R}. \tag{15}$$

Equation (14) gives us the rate of evaporation of tungsten as a function of the temperature. There are two empirical constants A' and λ_0 to be determined from the experiments.

Experiments on the Rate of Evaporation of Tungsten in Vacuum.

Several sets of experiments were made to determine the rate of evaporation. In each case lamps were made up with tungsten filaments, and the filaments were heated for various times at various temperatures. The rate of evaporation was determined usually by both of two methods, namely by increase in resistance and by decrease in weight.

First Set.—Five tungsten lamps were made up with single loop filaments without supports. The length of the wire used ranged from 10.6 to 11.2 cm. and the diameter was .0162 cm. These lamps were set up on life test at an efficiency of one watt per maximum horizontal candle power and maintained at constant voltage. The initial candle power varied from 40 to 41 among the various lamps. These lamps were taken off test after 500 to 1,000 hours, broken open, and the filaments weighed.

Second Set.—Five lamps similar to the last with lengths of filament from 10.6 to 11.2, and of the same diameter as before were set up on test at 0.8 watt per maximum horizontal candle power and maintained at constant voltage. The initial candle powers ranged from 58.5 to 60.5. These lamps were taken off test after 200 to 300 hours, and the filaments were weighed.

Third Set.—Two lamps containing single loop filaments of wire .0122 cm. diam. were made up. The filament of the first was 11.1 cm. long. This lamp was set up at constant voltage at an original temperature of 2800° K. (determined by color). The readings taken at frequent intervals were:

Table I.

Time, Minutes.	Volts.	Amperes.	Candle Power.
0	23.6	2.94	164
14	23.6	2.93	—
21	23.6	2.93	153
56	23.6	2.89	124
72	23.6	2.88	112

The second lamp had a filament 14.3 cm. long. This lamp was set up by color at 3136° K. and kept at constant voltage. The characteristics were:

TABLE II.

Time, Minutes.	Volts.	Amperes.	Candle Power.
0	35.5	3.55	504
1	35.5	——	311
2	35.5	3.38	238
3	35.5	3.30	199

Fourth Set.—This set was made up at a later date than the previous ones, and the measurements were conducted with much greater care. Five lamps were made up from wire .00709 cm. diameter, each with a length of about 77 cm. mounted in six loops. These lamps were photometered and set up with the filaments at temperatures ranging from 2738 to 2925° K.

The voltage was adjusted at frequent intervals so as to keep the product $V\sqrt[3]{A}$ constant. (V = volts, A = amperes.) In this way, notwithstanding a considerable change in the diameter of the filament, the temperature is maintained constant. This is readily seen from the following reasoning. The energy radiated is proportional to the diameter whence the function VA/d (watts divided by the diameter) is a function of the temperature but not of the diameter. Similarly if the material of the wire is unaltered, the resistance is inversely proportional to the square of the diameter, hence Vd^2/A is a function of the temperature but not of the diameter. Therefore

$$\frac{V^2A^2}{d^2}\times\frac{Vd^2}{A}=V^3A$$

is a function of the temperature but not of the diameter. Hence if $V\sqrt[3]{A}$ is maintained constant the temperature must remain constant even when the diameter changes.

The weight of the wire before sealing into the lamps was found to be 0.764 mg. per cm. of length.

The lamps were run as follows:

TABLE III.

No.	Temp.	Initial Volts.	Initial Amps.	Time, Minutes.	Final Volts.	Final Amps.	Final Wt. Mg per Cm.
1	2738	195	1.182	233	198	1.129	
2	2825	208	1.240	111	213	1.157	0.676
3	2875	216	1.260	65	222	1.159	0.671
4	2925	230	1.310	40	238	1.184	0.656
5	2930	235	1.318	14.5	237	1.269	0.722

The temperatures were determined by comparison of the color of the light emitted from the filament with that of a standard lamp viewed through a special blue glass. The details of this method of estimating temperatures will be given in a subsequent paper. For the present it will suffice to say that the temperature scale is primarily based on the following formula

$$T = \frac{11{,}230}{7.029 - \log H}. \tag{16}$$

Here H is the intrinsic brilliancy of the filament in international candle power per sq. cm. (projected area). On this scale the melting point of tungsten is 3540° K.

The initial volts and amperes give the characteristics of the lamps as first set up (after two hours ageing of the filament at 2400° K.).

The final volts and amperes give the characteristics after being set up at the indicated temperature for the time given in the fourth column.

The final weight is the average weight per unit length as found by weighing several lengths of the filament on a delicate microbalance after breaking open the bulbs.

CALCULATION OF THE RATE OF EVAPORATION.

Let w_0 = the original weight of the wire per unit length,
w = the weight per unit length after the time t,
ρ = the density of the wire,
r = radius of the wire,
R_0 = its initial resistance per unit length,
R = its final resistance per unit length.

Then it is easily seen that

$$w = \pi r^2 \rho,$$

or

$$r = \sqrt{\frac{w}{\pi\rho}}. \tag{17}$$

Now the effect of the evaporation is to remove tungsten from the surface at a rate proportional to the extent of the surface. That is, the thickness removed per unit time is constant and equal to m/ρ. Therefore

$$\frac{m}{\rho} = \frac{r_0 - r}{t} = \frac{\sqrt{w_0} - \sqrt{w}}{t}\,\frac{1}{\sqrt{\pi\rho}}, \tag{18}$$

whence

$$m = \sqrt{\frac{\rho}{\pi}} \cdot \frac{\sqrt{w_0} - \sqrt{w}}{t}. \tag{19}$$

This equation gives the rate of evaporation m in terms of the density and weight per unit of length of the filament.

Since the resistance is inversely proportional to the cross-section we have

$$\frac{R_0}{R} = \frac{w}{w_0}. \tag{20}$$

Substituting this in (19) gives

$$m = \sqrt{\frac{\rho}{\pi}} \sqrt{w_0} \cdot \frac{1 - \sqrt{\frac{R_0}{R}}}{t}, \tag{21}$$

from which m can be calculated from the changes in resistance.

It should be noted, however, that (20) assumes that the specific resistance remains unaltered, therefore equation (21) applies only when the filament is kept at constant temperature, as for example in the fourth set of experiments. In the first three sets of experiments, on the other hand, the lamps were run at constant voltage. The temperature therefore gradually decreases, and for this reason the resistance does not increase as rapidly as if the filament were kept at constant temperature. From data on the characteristics of tungsten filaments available in this laboratory it has been calculated that at constant voltage a 1 per cent. decrease in current corresponds to a decrease in cross-section of 1.11 per cent. or an increase of 1.11 per cent. in resistance at constant temperature. Therefore, before applying equation (21) to the data in the first three sets of experiments an 11 per cent. correction should be made in the changes in the resistance that are produced by the evaporation.

In calculating m from equations (19) or (21) the value of ρ was taken to be 19.4 which gives for $\sqrt{\rho/\pi}$ the value 2.486 in gram cm. units.

In calculating the values of m from the data of the fourth set of experiments, the values of $\sqrt{R_0/R}$ were plotted as a function of t and the best representative straight line was drawn among them. The slope of this line was used to calculate m according to equation (21).

RESULTS OF EXPERIMENTS.

The values of m, *i. e.*, the rate of evaporation of tungsten in grams per sq. cm. per second, were calculated by equations (19) and (21) as described above, and are tabulated below (Table IV.).

In order to determine whether m, the rate of evaporation, varies with the temperature according to the theoretical equation (14) the quantity $\log m + 1.4 \log T$ (column VI.) was plotted (Fig. 1) against $1/T$ (column V.).

According to equation (14) the points should lie along a straight line. Reference to Fig. 1 will show that the agreement is excellent, although the values of m vary in the ratio 1 : 15,000.

TABLE IV.

I. Set.	II. Lamp.	III. Temp. of Fil. °K.	IV. $m \times 10^6$.	V. $\frac{1}{T} \times 10^6$.	VI. $\log m + 14 \log T$.	VII. Method.
I.	—	2440	0.0020	409.8	6.05–10	Weight.
II.	—	2522	0.0059	396.5	6.53–10	"
III.	1	2800	0.39	357.1	8.42–10	Resistance.
"	2	3136	30.	318.9	0.38—	"
IV.	1	2738	0.151	365.2	7.99–10	"
"	2	2825	0.52	354.0	8.54–10	"
"	2	2825	0.59	354.0	8.59–10	Weight.
"	3	2875	1.01	347.8	8.84–10	Resistance.
"	3	2875	1.14	347.8	8.90–10	Weight.
"	4	2925	1.73	341.9	9.10–10	Resistance.
"	4	2925	2.33	341.9	9.23–10	Weight.
"	5	2930	1.84	341.3	9.13–10	Resistance.
"	5	2930	2.45	341.3	9.25–10	Weight.

The values of *m* determined by the change in resistance are in every case lower than those found from the change in weight. This is due to the fact that the elimination of traces of impurities from the tungsten by volatilization and a slow sintering process tend to decrease the specific resistance of the tungsten and hence counteract the increase in resistance due to evaporation. In fact, in the first and second sets of experiments at 2440 and 2520° respectively, the resistance during the first part of the life actually *decreased*, so that the resistance measurements are totally unreliable as a source of information about the rate of evaporation. At higher temperatures, however, these changes in specific resistance take place much more rapidly than at lower temperatures, and the resistance measurements become of greater significance.

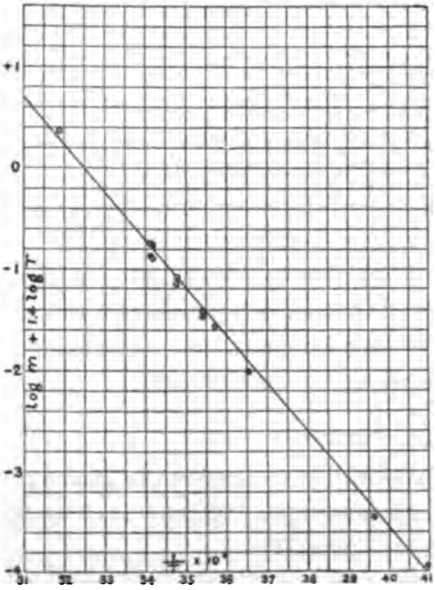

Fig. 1.

The values of *m* found from the changes in resistance are therefore probably not as accurate as those found from the loss of weight, but nevertheless serve as a very valuable check on the latter.

From the slope of the straight line in Fig. 1 we obtain

$$0.218\lambda_0 = 47{,}440,$$

whence

$$\lambda_0 = 217{,}800 \cdot g\text{—calories per mol.}$$

From this by (11) the heat of evaporation of tungsten at any temperature is $\lambda = 217{,}800 - 1.8T$.

We can also calculate the value of A', equation (14), from Fig. 1. We obtain

$$A' = 15.402.$$

Equation (14) thus becomes

$$\log m = 15.402 - \frac{47{,}440}{T} - 1.4 \log T. \tag{22}$$

From (15) we can now calculate A; equation (12) thus becomes

$$\log p = 15.502 - \frac{47{,}440}{T} - 0.9 \log T. \tag{23}$$

Since equation (22) represents the straight line on Fig. 1, it is readily seen that this equation gives a very satisfactory method of calculating the rate of evaporation at any temperature.

Similarly, if we may assume that the reflection of tungsten atoms from solid tungsten is small, then equation (23) must give the vapor pressure with a fair degree of accuracy.

In Table V. are given the rate of evaporation, and the vapor pressure of tungsten at various temperatures as calculated from equations (22)

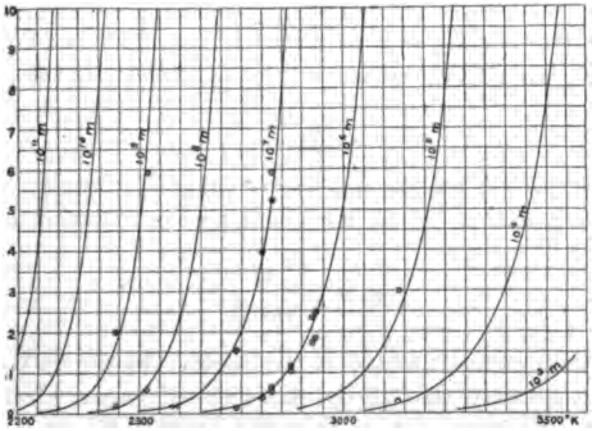

Fig. 2.

Rate of evaporation of tungsten in a vacuum (m = grams of tungsten per square cm. per sec.). Points experimentally determined (see Table IV.); curves calculated from equation (22).

Table V.

Rate of Evaporation and Vapor Pressure of Tungsten.

Absolute Temp.	Evaporation g per sq. cm. per sec.	Vapor Pressure, mm.
2000° K.	$114. \times 10^{-15}$	6.45×10^{-12}
2100	1.44×10^{-12}	83.2×10^{-12}
2200	14.4×10^{-12}	$849. \times 10^{-12}$
2300	116.7×10^{-12}	7.05×10^{-9}
2400	$798. \times 10^{-12}$	49.2×10^{-9}
2500	4.67×10^{-9}	$294. \times 10^{-9}$
2600	23.6×10^{-9}	1.51×10^{-6}
2700	$106. \times 10^{-9}$	6.95×10^{-6}
2800	$429. \times 10^{-9}$	28.6×10^{-6}
2900	1.57×10^{-6}	$106. \times 10^{-6}$
3000	5.23×10^{-6}	0.000362
3100	16.3×10^{-6}	0.00114
3200	46.7×10^{-6}	0.00333
3300	$126. \times 10^{-6}$	0.00910
3400	$320. \times 10^{-6}$	0.0234
3500	$769. \times 10^{-6}$	0.0572
(3540)	.00107	0.080
(5110)	——	760.

and (23). Above the melting point of tungsten the vapor pressure would follow another curve. The boiling point 5110° calculated from equation (23) must therefore be looked upon as a lower limit. However, since the heat of fusion of metals is very small compared to their heats of vaporization the error is certainly not large, and it can therefore be safely concluded that the boiling point of tungsten must lie in the neighborhood of 5100° K.

The data in Table V. have been plotted in Figs. 2 and 3. In Fig. 2 the rates of evaporation as determined by experiment (Table IV.) are plotted. It is seen that the equation (22) fits in well with the observations.

Summary.

1. It is shown that the vapor pressure (p) of a substance is related to its rate of evaporation (m) in a vacuum by the following relation:

$$m = \sqrt{\frac{M}{2\pi RT}}\,p,$$

where M is the molecular weight of the vapor. In the derivation of this equation it is assumed that all the molecules of vapor which strike the surface of the metal are condensed (not reflected). No other assumptions except those that have received ample experimental verification need be made.

2. Experiments were made to determine the rate of evaporation of tungsten in a vacuum at temperatures ranging from 2440° K. up to 3136° K. Over this temperature interval of 700° the rate of evaporation increased in the ratio 1 : 15,000.

3. From these data the vapor pressures were calculated and were found to agree excellently with the thermodynamical relations such as the Clausius-Clapeyron formula. The latent heat of evaporation of solid tungsten is thus found to be (per 184 grams)

$$\lambda = 217{,}800 - 1.8T \text{ calories,}$$

a value higher than the heat evolved by any known chemical reaction.

4. The rate of evaporation of tungsten at any temperature in a perfect vacuum is given accurately by the equation

$$\log_{10} m = 15.402 - \frac{47{,}440}{T} - 1.4 \log_{10} T;$$

here m is the rate of evaporation in grams per sq. cm. per second.

5. The vapor pressure of tungsten in mm. of mercury at the absolute temperature T is given by the equation

$$\log_{10} p = 15.502 - \frac{47{,}440}{T} - 0.9 \log_{10} T.$$

6. The vapor pressure of tungsten at 2400° K. the temperature of the filament in a lamp running at 1 watt per candle, is about 50×10^{-9} mm.

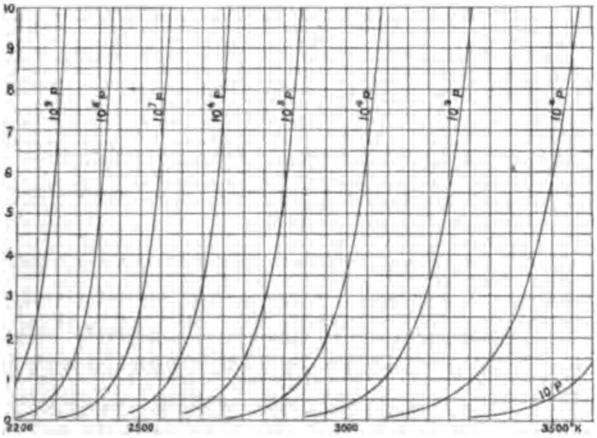

Fig. 3.
Vapor pressure of tungsten in millimeters of mercury.

At the melting point of tungsten, 3540° K., the vapor pressure is 0.080 mm. The boiling point of tungsten at atmospheric pressure is probably very close to 5100° K. The vapor pressure at other temperatures is given in Table V.

7. The rate of evaporation and the vapor pressure of tungsten are given in Table V. Curves of the same data are given in Figs. 2 and 3.

In subsequent papers the writer intends to publish data on the rates of evaporation and vapor pressures of platinum, carbon, molybdenum, tantallum, osmium, and some of the commoner metals such as copper, silver, nickel, and iron.

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THE INFRA-RED OPTICAL PROPERTIES OF SOME SULPHIDES: A BALANCED METHOD OF USING THE BOLOMETER.

By Irving B. Crandall.

THE relation between the optical properties of compounds and their chemical properties has been investigated for a number of substances in the visible and ultra-violet regions of the spectrum. Certain organic compounds have also been experimented with in the infra-red spectrum in a systematic manner, but little has been done in this region with classes of inorganic compounds (including minerals) if we except the work of Nichols and his students on the reflection from salts of the alkaline earths,[1] of Clark on the reflection from chromates,[2] of Morse on the reflection from carbonates,[3] of Rubens and Hollnagel on the reststrahlen from salts of the alkalies,[4] and of Coblentz on the rôle of water in minerals.[5] Perhaps the field seems unpromising on account of the difficulty of obtaining good pieces of the right dimensions of the solids in question, and polishing their surfaces.

Last year Prof. A. Trowbridge, noting the perfect cleavage in one direction of the minerals molybdenite and stibnite, was led to investigate the optical properties of thin layers of these substances. He used an infra-red spectrograph of moderate resolving power, and obtained approximate values for the extinction modulus $n\chi$ for the two substances. On observing the transmission of very thin cleavage layers of molybdenite there were found broad absorption bands, regularly spaced, beginning at wave-length 5 or 6μ. The same piece exhibited bands close together in the very short region in the red end of the visible spectrum for which it was transparent. It was not known whether these bands were due to interference in the layer, or simply to ordinary absorption. The object of undertaking the present investigation was to repeat these measurements with apparatus of larger resolving power, and determine, if possible, the refractive indices. In addition, it was planned to experiment with other sulphides, and discover any common optical properties that might exist. The position and magnitude of the bands shown by molybdenite were to receive especial consideration, as, if they proved to be due to interference, a way might be found to determine the refractive index that did not depend on the reflecting power. The refractive indices of molybdenite and stibnite were known to be very high[1] so that they should be interesting substances from this point of view alone. Before going further, we may remark that the sulphides are, next to the halogen salts and oxides, the simplest class of binary metallic compounds, and ought to give easily interpreted results.[2]

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[1] Phys. Rev., XXVII., 1908, p. 225, and other papers.

[2] Astro. Jour., 35, 1912, p. 48.

[3] Astro. Jour., 26, 1907, p. 225.

[4] Sitz. Ber. Preus. Akad. Wiss., Berlin, 4, 1910, p. 26.

[5] Jour. Fr. Inst., CLXXII., 1911, p. 309.

A Balanced Method of Using the Bolometer.

In the work to be hereinafter described the bolometer was used in a manner perhaps unusual, for comparing intensities of radiation in the infra-red spectrum; we therefore proceed to consider the method somewhat in detail.

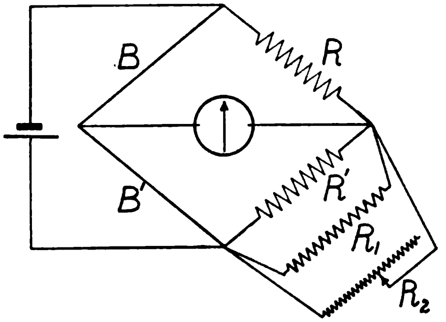

Fig. 1.

A linear bolometer of the usual form was constructed, the dimensions of the two strips forming two arms of the Wheatstone bridge being in width 0.5 mm. and in length 25 mm. These had a resistance of about 4 ohms each. The other two arms of the bridge were coils of manganin wire situated within the bolometer case, and having a resistance of 20 ohms each. The connections are as given in Fig. 1. A current of about 0.08 ampere traversed each arm of the bridge. The radiation is supposed to fall on the strip *B*.

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[1] See later references.

[2] After this work had been completed and prepared for publication, it was found that an important paper dealing with this subject, by J. Koenigsberger and O. Reichenheim (Centralbl. f. Min., 1905, p. 454) had been overlooked. These authors investigated the absorbing powers and electrical conductivities of molybdenite, stibnite, pyrite, galena, and iron sulphide; their work on conductivity furnishes the only data available for these materials, and will be quoted later in the discussion of the present results. On absorption, however, since they did not use spectral dispersion, but only employed screens to obtain comparatively large ranges of radiation—the total radiation in a given region of the spectrum being measured—their results are only approximate. These will be compared with those obtained by the writer for the various materials. Koenigsberger and Reichenheim state that they were usually only able to use small pieces (4×4 mm. in area) of the minerals: in the present work much larger pieces of stibnite and molybdenite were used, and they were also of quite uniform thickness; it must be stated, however, that Koenigsberger and Reichenheim have results for pyrite, which the present author found quite difficult to handle, so that no results are offered here for this material.

The bridge would ordinarily be balanced for zero radiation by shunting one of the arms, say R', with a more or less constant resistance R_1, and then, the bolometer strip B being exposed to the radiation, the deflection of the galvanometer deflection taken as directly proportional to the energy received by the strip. The present method, however, consists in balancing the bridge again by adjusting the shunt, and converting readings obtained in this way into relative changes of resistance in B, due to the incident radiation. If we determine the relative changes in the resistance of the strip produced by different quantities of energy falling on it, we have accurately the ratio between the two quantities of energy, if we make the single assumption (fundamental for all bolometric work) that the change in the resistance of the strip is directly proportional to the quantity of energy falling on it. If B were equal to B' and R to R' within very narrow limits, then a resistance of several thousand ohms as R_1 would suffice to balance the bridge; furthermore, a change of 0.1 ohm in R_1 would probably be the smallest convenient amount which would be detected by a good galvanometer, say of 10 ohms resistance and a sensitiveness of 10^{-9} ampere per scale division at a meter distance. In the present case however the strips B and B' were hurriedly made, and only adjusted to within about 1.5 per cent. of each other, so that it became necessary to use R_1 for balancing the bridge for zero radiation, and to add the supplementary resistance R_2 for the purpose of making the adjustments used in measuring the radiation.

For the sake of completeness we give here the numerical calculations relating to a definite set of values for the various resistances used. Several combinations were tried, but the one which seemed best adapted to the sensitiveness of the galvanometer was the following:

$B = B' \pm 1.5$ per cent. = ca. 4 ohms,
$R = R' = 20$ ohms,
$R_1 = 588$ ohms,
$R_2 = 4{,}800$ ohms (variable by increments of 0.1).

Given different changes in R_2 corresponding to different values of the resistance of the arm of the bridge (or different quantities of energy falling on B) we desire the relation between them. If the total resistance of the arm is denoted by R, then

$$\frac{1}{R} = \frac{1}{R'} + \frac{1}{R_1} + \frac{1}{R_2} = \frac{R_1 + R'}{R_1 R'} + \frac{1}{R_2} = a + \frac{1}{R_2}, \tag{1}$$

where $a = (R_1 + R')/(R_1 R')$ is kept constant. Differentiating,

$$dR = \frac{dR_2}{(R_2 a + 1)^2}, \tag{2}$$

which shows at once that dR_2 is quite different for equal changes dR if we consider two changes dR which are the first and last increments in a total change of, say, $100dR$. We must therefore derive a convenient formula for correcting the observed readings dR_2: one would naturally expect that an additive per cent. correction would be easiest to apply to dR_2. Since dR_2 is now no longer an infinitesimal, but a considerable fraction of R_2 we must derive the formula rigorously from the beginning. Writing down (1) and increasing R and R_2 by dR and dR_2 respectively, we have

$$R = \frac{R_2}{1 + R_2 a}, \tag{3}$$

$$R + dR = \frac{R_2 + dR_2}{1 + (R_2 + dR_2)a}, \tag{4}$$

whence

$$dR = \frac{R_2 + dR_2}{1 + (R_2 + dR_2)a} - \frac{R_2}{1 + R_2 a}, \tag{5}$$

$$= \frac{dR_2}{(R_2 a + 1)^2 + a dR_2(1 + aR_2)}, \tag{6}$$

for which we may write

$$dR = \frac{dR_2}{(R_2 a + 1)^2}(1 - x), \tag{7}$$

in which x denotes the required per cent. correction. Equating the right-hand members of (6) and (7), we find that

$$x = \frac{a dR_2}{(1 + aR_2) + a dR_2}. \tag{8}$$

As $|a dR_2| < |1 + aR_2|$ we note that if dR_2 is negative, x is negative and therefore the correction is additive. To apply the correction, we first calculate

$$a = \frac{R_1 + R'}{R_1 R'} = \frac{1}{R'}\left(1 + \frac{R'}{R_1}\right).$$

Since a is approximately $1/R'$, or $1/20$, x is very nearly independent of a, and this approximate value of a is quite good enough to use in computing x. If we compute x as a function of dR_2 we have the following values which are plotted in Fig. 2.

$$\frac{1}{a} = R' = 20 \text{ ohms.} \quad R_1 = 588 \text{ ohms.} \quad R_2 = 4{,}800 \text{ ohms.}$$

dR_2	$-x = \dfrac{-dR_2}{R' + R_2 + dR_2}$
− 100 ohms	+0.021
− 400	0.091
− 800	0.199
−1200	0.331

We can easily read from the curve the proper correction to apply to a given reading; *e. g.*, if dR_2 is 1,200 ohms we add 33 per cent. or multiply by 1.33 to obtain a number directly proportional to the change in resistance of an arm of the bridge. Assuming that the change in resistance is directly proportional to the energy falling on the strip, we then have a number directly proportional to this quantity of energy. Note in passing that, in case R_2 shunted an adjacent arm of the bridge and had to be increased, the correction would be a negative one, and relatively decreasing with increasing dR_2, *i. e.*, concave to the right instead of to the left.

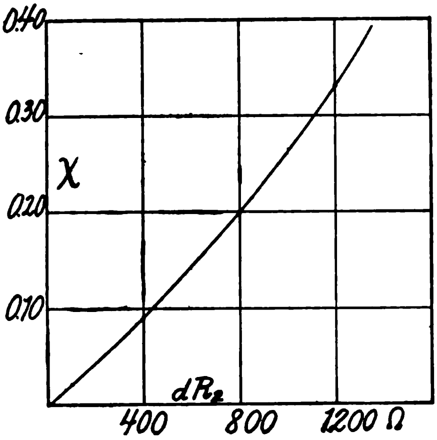

Fig. 2.

The following points in favor of this method of using the bolometer may be noted:

It does not assume that the current through the galvanometer is directly proportional to the change in the resistance of one of the bridge arms.

It is independent of changes in the sensitiveness of the galvanometer, and also of the position of the galvanometer zero, if this varies.

In passing through parts of the spectrum rich in energy, there is no abrupt change in the sensitiveness of the apparatus to radiation, as there would be if successive shunts or series resistances had to be thrown into the galvanometer circuit. In fact the double uncertainty of non-linear galvanometer scale and inaccurate shunts was what led the writer to try this balanced method. The non-linear scale, in particular, is a great disadvantage, which can scarcely be avoided as long as we have to use for measuring radiation galvanometers with small suspended system turning through relatively large angles. For these reasons this method should be peculiarly adaptable to running energy-spectrum curves.

Under favorable conditions as to steadiness of bolometer (using a very tightly enclosed vacuum-bolometer) one could easily read the energy at the maximum of an energy curve to one ten-thousandth part of itself. This condition was realized by the present writer, in the following measurements, as far as quantity of energy and sensitiveness was concerned, but not with regard to steadiness, as the bolometer was air enclosed, and, in passing through the spectrum, the zero (that is, the value of R_2 necessary to balance for no radiation falling on the strip) was not determined after each reading, but only at intervals over the whole range. It takes time and patience to balance the bridge, but when accurate results are desired, it seems that this method may be valuable, although where the energy curve is flat and the quantity of energy relatively small (say for $\lambda > 10\mu$) it must be said that the deflection method yields about as accurate, and rather more easily obtained results.

ARRANGEMENT AND ADJUSTMENT OF THE OPTICAL APPARATUS.

The infra-red dispersion apparatus consisted of a rock-salt prism of angle 60° 1′ 8″ and faces 11 cm. by 7.5 cm. high, fitted with a Wadsworth mirror, the whole rotating with the 17-inch divided circle of a large spectrometer of the ordinary type. Two concave mirrors of 66 cm. focal length and 7.5 cm. aperture served as collimators, being rigidly mounted on arms of the spectrometer. The bolometer case was held by an independent massive support, as were also the slit and an external mirror (of 7.5 cm. aperture and 33 cm. focus) which was used to bring a real image of the source of light on the slit. When not in use a glass cover jar was fitted over the prism, and sealed with oil in an annular trough around the edge; a drying agent placed within assured a dry atmosphere surrounding the prism. This arrangement has been very satisfactory for a period of time of several months. The whole apparatus, then, does not differ from the ordinary infra-red prism spectrograph except perhaps in point of size.

The width of the bolometer strip has been given as 0.05 cm.; in most of the following work the slit was of the same width, and its length was such that the spectrum covered nearly all of the bolometer strip. In a few cases, however, the proportions of the slit were changed in order to try the transmission of a small specimen. A slit of width 0.05 cm. subtends an angle of 0.00076 radians or 2.7 minutes of arc, if viewed from the telescope mirror. This is equal to an extent in the spectrum of from 0.1μ to 0.5μ, depending on the dispersion. On the average, between 1μ and 7μ the strip may be considered as receiving the energy of a spectral region 0.25μ in extent.

For calibration, the D line was taken as a datum, and a curve was plotted showing the deviation from the position of the D line as a function of λ. The prism angle was carefully measured, and for the dispersion of the rock-salt, Paschen's[1] values were used. From the deviation curve, a scale of wave-lengths and angular rotation from the D line was constructed by projection on the drawing board. This scale was about 12 inches long for the region from $\lambda = 0.5896\mu$ to $\lambda = 7\mu$. For making the measurements rapidly, advantage was taken of a train of gears which connected the rotating prism-circle with a plate lowering apparatus, which was originally designed so that infra-red bolograms could be made by recording the galvanometer deflections on a moving sensitive plate. The graphically constructed scale was of such a length that when fitted to the plate-carrier (the whole apparatus being adjusted to the D line), the scale slid by a fiducial mark giving correct wave-length readings as the spectrum was made to march across the bolometer strip. A test of the scale usually gave the wave-length of the CO_2 absorption band within 0.02 or 0.03μ of its correct value ($\lambda = 4.38\mu$). Of course settings made with this scale cannot compare for accuracy with those made by means of a calibration curve and a reading microscope, but this would have been very tedious work for these measurements. The various gears between the plate carrier and the rotating circle introduced small errors of lost motion and uneven running which could not be eliminated. Taking into consideration all errors, it is estimated that the absolute position in the spectrum at any setting was known, on the average, to within 0.05μ, and any setting could be repeated (by turning back, and coming forward again until the same division was under the mark) to about 0.01μ. Some badly determined points may be noticed among the observations: the steep slopes of the energy curve near the atmospheric absorption bands at 2.1μ, 2.7μ, and 4.4μ were especially troublesome, and inaccuracies due to this cause cannot be avoided unless a setting can be repeated to within a few thousandths of a μ, which was impossible with the method and apparatus used by the writer.

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[1] Ann. d. Physik, 26, 1908, p. 128.

As a source of light, a one-ampere A.C. Nernst filament operated somewhat below full capacity on a storage battery, was found to give the most constant radiation. After being used for some time, the A.C. glower (with leads fused in at each end) seemed to develop a very constant resistance. It may be stated that enclosing the source of radiation in a water jacket proved very effective for disposing of all the energy not thrown into the spectrometer by way of the collimating system.

No limiting diaphragm was used anywhere in the path of the beam. Practically, the prism face acted as such a diaphragm, as the beam from the collimator was so much larger than the prism face that the prism refracted only about 50 or 60 per cent. of the light, that is, the central portion. Since the light from the edges of the mirrors was thus lost, small errors in collimation, introduced by interposing specimens, had practically no effect on the position and intensity of the spectrum.

THE OBSERVATIONS.

In determining the per cent. of light transmitted through, or reflected by a given specimen, settings were made at intervals of about 0.1μ throughout the spectrum, and readings taken with the bridge balanced at each setting—thus obtaining measures of the relative quantities of energy at different wave-lengths. Then the spectrometer was turned back, the specimen interposed, the same settings repeated and the energy determined as before. The ratio was easily computed after the corrections earlier described were applied to the bridge readings.

If natural specimens are used it is hardly practicable to place them in parallel light; they must be placed where the beam is small, *i. e.*, near the slit. All the transmission specimens used by the present writer were placed perpendicular to the beam, and *behind* the slit. It is especially important for specimens of highly refracting material that they be placed, behind rather than in front of the slit, in order that the focus of the image of the energy-source on the slit shall be exactly the same with and without the specimen in place. For reflection the arrangement shown in Fig, 3 was used: the silvered mirrors M_1 and M_2 were fixed, and the mirror M, also silvered, could be removed and a surface of the material to be investigated substituted. The angle of incidence was here about 18°, which was practically normal incidence for materials of high refractive index. The reflecting power of the specimen was easily determined, using Hagen and Rubens'[1] values for the reflecting power of silver to correct the energy observed when mirror M is in place.

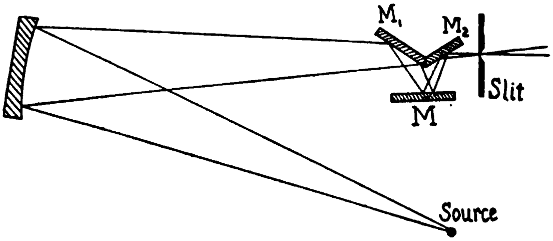

Fig. 3.

THE OPTICAL PROPERTIES OF SOME SULPHIDES.

Stibnite.—The observations on stibnite are given in Fig. 4. Two determinations were made of the reflection, and of the transmission of two different thicknesses. The curves are simply a mean, intended to be as consistent as possible with both sets of observations. This practice was followed with all the observations.[1]

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[1] Ann. d. Physik, 11, 1903.

Specimens of Japanese stibnite were used with natural, fresh cleavage surfaces. Stibnite crystallizes in the orthorhombic system, and is biaxial if like all known transparent crystals of this class. The cleavage is perpendicular to the crystallographic *b*-axis, so that the path of the light lay along this axis. The bisectrix of the optical axes of crystals of this type may lie along any one of the *a*, *b*, *c*, crystallographic axes, so that the optical constants here determined are for neither pure ordinary or extraordinary rays. They are offered merely as empirical relations which will have to serve for cleavage layers until this substance is more thoroughly investigated.[2] In Fig. 8 are given the values of the extinction-

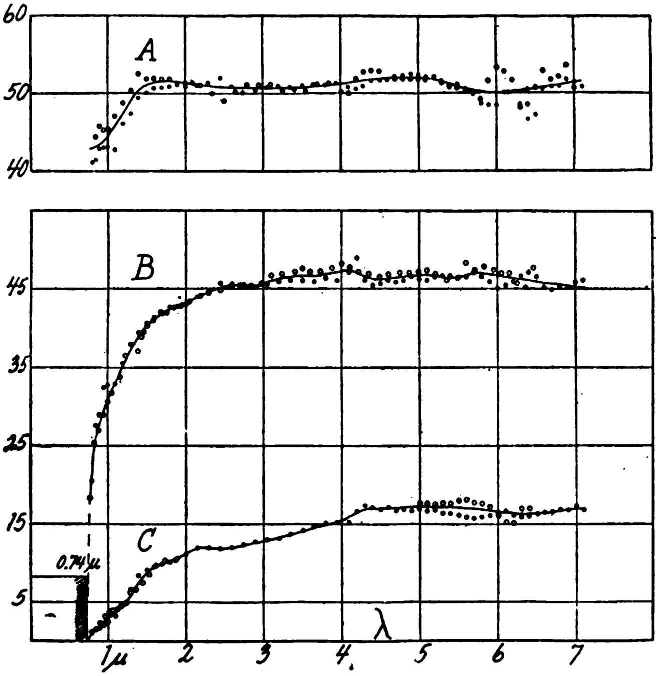

Fig. 4.

Curve *A*: Per cent. of energy reflected from stibnite.
Curve *B*: Per cent. transmitted through layer 0.18 cm. thick.
Curve *C*: Per cent. transmitted through layer 0.73 cm. thick.

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[1] Koenigsberger and Reichenheim obtain somewhat lower values for transmission and reflection of stibnite. Coblentz, however (quoted in Wood's Optics, 2d ed., p. 400), obtains a value for transmission very close to that offered here.

[2] The following experiments by Prof. A. Trowbridge on the double refraction of stibnite may be of interest here:

A collimator system containing a glass lens, a slit, and a concave mirror was set up between modulus[1] $n\chi$ computed from the observations on the transmission of the two thicknesses by means of the formula

$$n\chi = \lambda\alpha = \frac{\lambda \log J_1/J_2}{4\pi(d_1 - d_2) \log e}$$

in which α = the extinction coefficient,
J_2 = relative transmission of the thin piece,
J_1 = relative transmission of the thick piece,
d_1 = thickness of thick piece, and
d_2 = thickness of thin piece, measured with the micrometer caliper.

In the derivation of this formula the reflection from the first surface and one reflection from the last surface are eliminated. If a specimen acts as a Fabry and Perot interferometer, and by successive internal reflections contributes to the transmitted energy, we can only observe that on account of the thickness the resulting interference bands in the spectrum are so narrow that the bolometer does not resolve them, and only the mean energy is observed. This should be equal to the energy in the first transmitted ray, so that we are justified in placing confidence in the above given formula; furthermore the successive rays due to multiple internal reflections are rapidly extinguished by the increased absorption due to lengthening path in the material.[2]

The limit of transmission of a piece a fraction of a millimeter thick is at 0.74μ.[3]

a Nernst filament and a bolometer. In this collimator system were placed an analyzer and a polarizer consisting of transmission plates of mica, with their directions of greatest transmission crossed. Between analyzer and polarizer was placed a layer of stibnite which was rotated. There was no dispersion, total radiation through the glass lens being measured by the bolometer. On the stibnite cleavage surfaces there are striæ parallel to the crystallographic a-axis: it was found that when the layer was turned so that the striæ made an angle of 45° with the plane of polarization of the polarizer, about four times as much energy was transmitted as when the striæ were either perpendicular or parallel to the plane of polarization. This shows either that it is more transparent to a vibration making an angle of 45° with the striæ, or that in that case it gives rise to a circular vibration: either explanation would imply double refraction.

Again, the polarizer was removed, and a prism placed in the collimator system, thus converting it into a dispersion apparatus. The layer of stibnite was put in with its striæ parallel to the slit, and energy spectra observed with the analyzer set at different azimuths. It was found for wave-lengths less than 3μ (for which the glass lens was transparent) that more energy got through when the plane of vibration of the analyzer was parallel to the striæ than when perpendicular. This shows that its extinction coefficient is different for vibrations in different directions, or, that it acts like tourmaline to some degree, and may be used as an analyzer.

[1] We follow the notation of Kayser, Handbuch, III., p. 15.

[2] Koenigsberger and Reichenheim (loc. cit.) derive a more rigorous formula, taking into account the second reflections, but we do not carry the formula this far, for the reasons stated.

[3] A piece of stibnite transparent down to 0.7500μ at ordinary temperature became transparent to 0.7200μ on being cooled by immersing in liquid air.

No attempt to obtain the refractive index was made except in a very general way from the reflection observations. After 4μ the reflection and absoprtion curves are practically constant: since the value of $n\chi$ is so very low, we may obtain an approximate value for the refractive index by ignoring $n\chi$ and using the formula for reflecting power

$$R = \left(\frac{n-1}{n+1}\right)^2, \tag{9}$$

which, solved for n, gives

$$n = \frac{1}{1-R}(1 + R \pm \sqrt{4R}). \tag{10}$$

Using the larger root for n we calculate the following values:

λ	n
1.5μ	6.00
3.0	5.95
5.0	6.16
7.0	5.97

which are given simply as being in the neighborhood of those given by E. C. Müller, namely $n_{\text{red}} = 4.69$ and $n_{\text{blue}} = 5.53$.[1] The outstanding feature is of course the very small dispersion, and the constancy of the extinction coefficient α from about 2μ on, in the infra-red.

On the electromagnetic theory for absorbing bodies the relations[2]

$$n^2(1 - \chi^2) = \epsilon, \tag{11}$$

$$N^2\chi = \sigma T, \tag{12}$$

should hold, in which ϵ is the dielectric constant, σ the conductivity in absolute electrostatic units, and T the time of one vibration. The writer is unable to find any data for the two electrical constants, but the following table, calculated from the values of n and $n\chi$ may be of some use (we take n = 6.00 for these values of λ):

λ	n	$n\chi$	$\sigma = n^2\chi/T$
1.5μ	6.0	3.35×10^{-5}	4.0×10^{10}
3.0	6.0	5.6 10^{-5}	3.3 10^{10}
5.0	6.0	7.2 10^{-5}	2.6 10^{10}
7.0	6.0	10.0 10^{-5}	2.6 10^{10}

A conductivity of 3×10^{10} electrostatic units is equal to a resistance of 30 ohms per cubic centimeter.

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[1] Wood, Physical Optics, 2d ed., p. 400.

[2] Drude, Lehrbuch d. Optik, 2d ed., p. 341.

Sphalerite.—The observations on this substance, the natural sulphide of zinc, are given in Fig. 5. Sphalerite is isometric (optically isotropic) and all cleavages should give specimens with the same optical properties. The material is marred by a yellow coloring and resinous streaks due to the presence of iron and manganese sulphides, which crystallize isomorphous with the sphalerite. With regard to the curves, the crossing of *B* and *C* at $\lambda = 4.5\mu$ may be explained by the fact that *B* is from a very small specimen, which necessitated using a short and wide spectrometer slit in running the curve. *B* is offered simply for its interest near the absorption band at 3.2μ. The fact that *D* is so much lower than *C* for $\lambda < 3\mu$ is probably due to a much greater quantity of the brown impurity in the thick specimen. The values of $n\chi$ computed from curves *C* and *D*

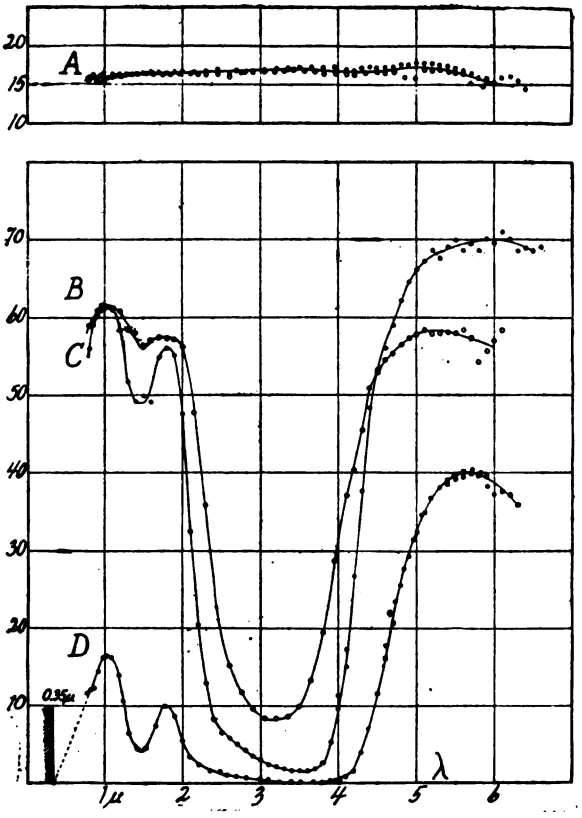

Fig. 5.

Curve *A*: Per cent. of energy reflected from sphalerite.
Curve *B*: Per cent. transmitted through layer 0.067 cm. thick.
Curve *C*: Per cent. transmitted through layer 0.253 cm. thick.
Curve *D*: Per cent. transmitted through layer 1.68 cm. thick.

are given in Fig. 8. The limit of transparency of a piece about 0.5 mm. thick was determined by the writer with the aid of an ultra-violet spectrograph and found to be about at 0.35μ. It is practically impossible to determine the refractive index of sphalerite in the infra-red without polishing acute prisms of the material. Experiments made by the writer show that a polish even approaching the perfection of a cleavage surface is out of the question, as the material is comparatively soft; its hardness on the Moh scale being about 3.7. The refractive index is so high ($n_{\text{green}} = 2.4007$, $n_{\text{yellow}} = 2.3692$, $n_{\text{red}} = 2.3417$[1]) that natural cleavage prisms (of angle 60°) are of no use, even if they could be obtained of sufficient size.[2]

The absorption bands determined at 1.5μ and 3.2μ should be characteristic of pure sphalerite. According to numerous analyses, no water of crystallization or of combination is contained in the material.

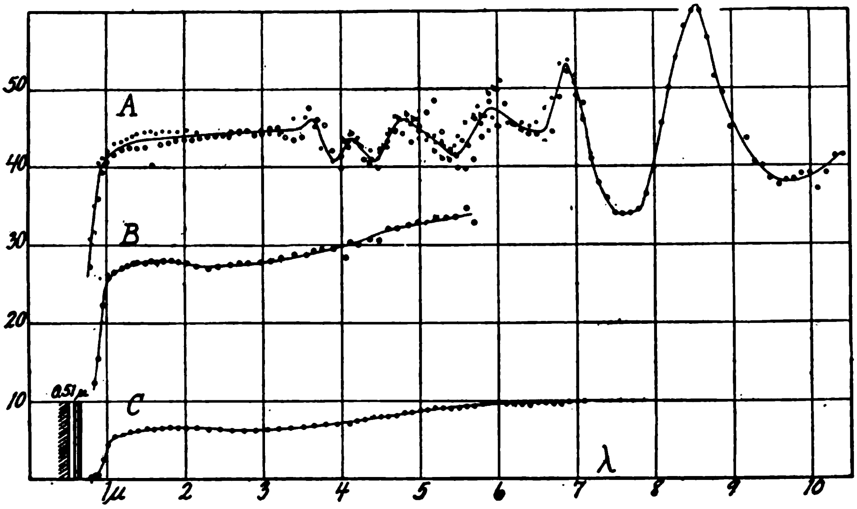

Fig. 6.

Molybdenite.

Curve A: Per cent. transmission of a layer 4.2μ thick.
Curve B: Per cent. transmission of a layer 0.0246 cm. thick.
Curve C: Per cent. transmission of a layer 0.0769 cm. thick.

Molybdenite.—This is the most interesting of all the sulphides in its optical properties. Its crystals are hexagonal, with basal cleavage allowing specimens of almost any thinness to be obtained. Hexagonal crystals are doubly refracting, uniaxial with the optic axis along the crystallographic *c*-axis, that is, perpendicular to the cleavage planes. Therefore in determining the optical constants for light passing along the optic axis, we have to deal only with the ordinary ray, and any constants that we can determine in this way are the true ones for the ordinary ray. The observations for the relative transmission are given in Fig. 6. The wavy character of Curve *A* is very striking and at once suggests interference. That this is interference is proved by the fact that the spacing of the bands varies with the thickness of the specimen. In Fig. 7 Curve *A* gives the energy reflected from a piece slightly thicker;[1] the bands are closer together, as they should be.

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[1] Ramsay, Zt. f. Kryst., 12, 1887, p. 218.

[2] We have no data that will enable us to test the relation $n^2\chi = \sigma T$. Doelter (Sitz. Ber. d. Kais. Akad., Wien, 119, I., 1910, p. 49) states that "zinc sulphide, even when heated to 420° (when it decomposed) showed practically no conductivity."

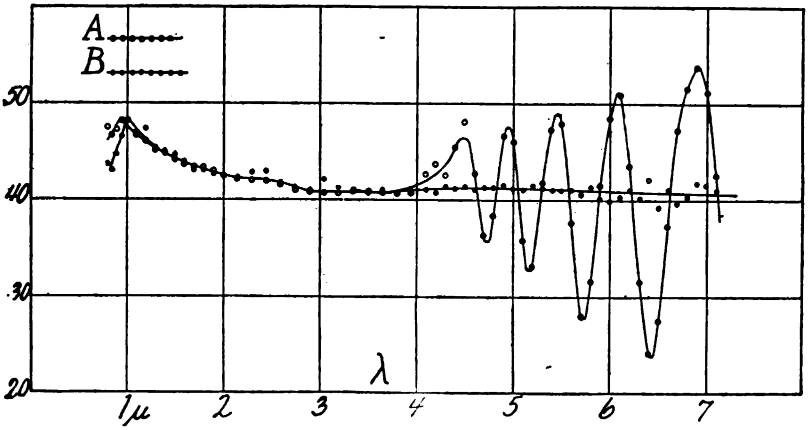

Fig. 7.

Molybdenite.

Curve *A*: Per cent. of energy reflected from a layer 6.6μ thick.

Curve *B*: Per cent. of energy reflected from a layer 34μ thick.

Both of these also showed interference in the visible region as will be discussed later. A very thin specimen (about 1μ thick) gave the absorption spectrum shown in the lower left-hand corner of Fig. 6, the limit of transmission being at about 0.51μ. Besides the 3 curves shown in Fig. 6 a fourth might have been given showing the transmission of a piece 34μ thick, but this is omitted, as it is practically identical with Curve *A* except in the matter of interference. The light reflected from this piece is given in Curve *B*, Fig. 7, which is also identical with *A*, Fig. 7, except for the interference. The values of $n\chi$ given in Fig. 8 are computed by the usual method from Curve *A* (using mean values where it oscillates) and Curve *C*, Fig. 6.

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[1] Koenigsberger and Reichenheim (op. cit.) give a reflecting power for molybdenite much lower than this.

The determination of the thickness of the very thin pieces of molybdenite is somewhat difficult by ordinary methods. Any method involving pressure is apt to damage the specimen, so that recourse was had to the method of weighing, the specific gravity having been determined and the area of the piece being computed.

To produce a good cleavage surface for reflection, it was necessary to split a thin layer of the material and squegee it down onto a piece of plate glass by rubbing it lightly with a pad of cotton, thus securing a fairly plane surface and good definition.

We proceed to consider the interference phenomena exhibited by the thin layers of this material. When a thin film is placed in front of the slit of a spectrometer, the positions and the spacing of the resulting interference bands in the spectrum afford a means of finding the dispersion of the material of the film. For a dark band at λ_1 the following relations must hold:

$$2n_1t = (N_1 + \tfrac{1}{2})\lambda_1;$$

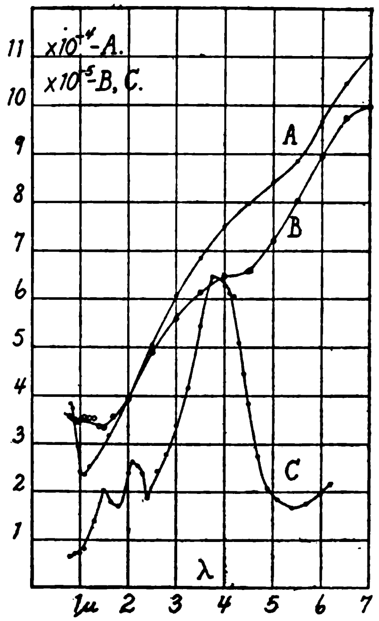

Fig. 8.

Curve *A*: $n\chi$ for molybdenite.
Curve *B*: $n\chi$ for stibnite.
Curve *C*: $n\chi$ for sphalerite.

similarly for a dark band at λ_2

$$2n_2t = (N_2 + \tfrac{1}{2})\lambda_2, \tag{14}$$

in which n is the refractive index, N a certain integer, and t the thickness of the film. For neighboring bands, that is, for two values of λ close together, we assume that dispersion is not an important factor, and consider that the bands occur simply on account of the varying relation between λ and $2nt$; we may then take $n_1 = n_2 = n$ and easily derive the following formula from (13) and (14) by subtraction:

$$N = 2nt\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right), \tag{15}$$

in which $N = N_1 - N_2$, the change in N_1 in passing from λ_1 to λ_2, and is equal to the number of bands between λ_1 and λ_2. This may be written

$$n = \frac{N\lambda_1\lambda_2}{2t(\lambda_2 - \lambda_1)}. \tag{16}$$

The formula is only approximate on account of the real variation of n with λ, but it will be seen that if n varies slowly it should hold over short ranges; moreover, if n should vary rapidly and *increase* as λ *decreases* the bands will naturally come close together, so that we might even use it in this case, if we take only one or two bands as an interval.

We give the following data on the position of interference minima for films of various thicknesses. The infra-red observations are from Curve *A*, Fig. 7, and Curve *A*, Fig. 6. The observations in the visible region were made with the aid of a Hilger wave-length spectrometer and are means of several settings. The bands should of course be regularly spaced from the visible on into the infra-red region; since however the width of the bolometer strip was such that in the region from 2–3μ it covered an extent of about 0.5μ in the spectrum, the bands are so closely spaced that they cannot be resolved.

	Transmission.		Reflection.
Thickness	(1) 4.2μ.	(2) 2.2μ.	(3) 6.6μ.
Positions of interference minima....	0.7141 μ	0.7001 μ	
	0.7208	0.7101	
	0.7286	0.7228	
	0.7361	0.7379	
	0.7453	0.7557	
	0.7555	0.7751	
	0.7658		
	0.7759		
	——	——	——
	3.45		4.75
	3.95		5.18
	4.45		5.75
	5.40		6.45
	6.45		7.38
	7.65		
	9.80		

Applying the formula successively to the visible readings in set (1) taking two fringes as the interval, and to set (2), taking 1 fringe at a time, and taking for λ the mean of λ_1 and λ_2, we compute the following:

λ	n Set (1).	n Set (2).	λ	n Set (1).	n Set (2).
0.7050		11.3	0.7453	6.84	
0.7164		9.17	0.7468		7.12
0.7208	8.54		0.7555	6.63	
0.7286	8.25		0.7654		6.87
0.7304		8.02	0.7658	6.85	
0.7361	7.74				

Assuming that n is practically constant between $\lambda = 3.5\mu$ and 10μ, as reflection and transmission curves are horizontal here, and calculating a mean value of n, using the first and last only of the infra-red observations, we have

From set (1), $n = 4.2$
From set (3), $n = \underline{4.04}$
Mean 4.1

In order to utilize the single readings we observe that the difference in optical length of path which gives rise to the interference is for the transmission piece (1) $2nt$ or about 34.4μ and for the reflection piece 54.3μ. For transmission the path difference should be equal to an odd number of half wave-lengths, and for reflection, an even number (taking into account the phase change of $\lambda/2$ of the directly reflected ray) in order to produce a minimum. By trial the following numbers are found to satisfy this condition approximately, and on assuming that they do exactly, the retardation $2nt$ can be calculated for a given value of λ and hence a value of n_λ found, $2t$ being known.

Set (1) Transmission.				Set (3) Reflection.			
λ	Number, N.	$N\lambda = 2nt$.	$\therefore n$.	λ	Number, N.	$N\lambda = 2nt$.	$\therefore n$.
3.45	9.5	32.8	3.9	4.75	11	52.3	3.98
3.95	8.5	33.5	4.0	5.18	10	51.8	3.95
4.45	7.5	33.4	4.0	5.75	9	51.8	3.95
5.40	6.5	35.1	4.2	6.45	8	51.6	3.93
6.45	5.5	35.4	4.2	7.38	7	51.6	3.93
7.65	4.5	34.4	4.1				
9.80	3.5	34.3	4.1				

We now have approximate values for n over a short range of the visible and a considerable region of the infra-red. The dispersion is given in Fig. 9, Curve A; a larger scale is used for the values in the visible region. In drawing the curve more weight is given to the values from set (3) on account of the very accurate spacing of the interference bands in the reflection-specimen. The transmission specimen is undoubtedly of slightly varying thickness, which accounts for the relatively poor determination of the interference bands observed. By weighing, of course, only a mean thickness is determined. With regard to the accuracy of the method, it should give good results under favorable conditions: that is, with a perfect Fabry and Perot interferometer in front of the infinitely narrow slit of a perfect spectrometer. At any rate, allowing for the unevenness of films, wide slits, etc., which are unavoidable with these specimens, the values of n should be correct within 5 or 10 per cent. From the reflection curve, taking the limiting value of 41 per cent. reflected light, and using formula (10), we compute $n = 4.5$ which is not far from the value obtained by means of the interference observations.

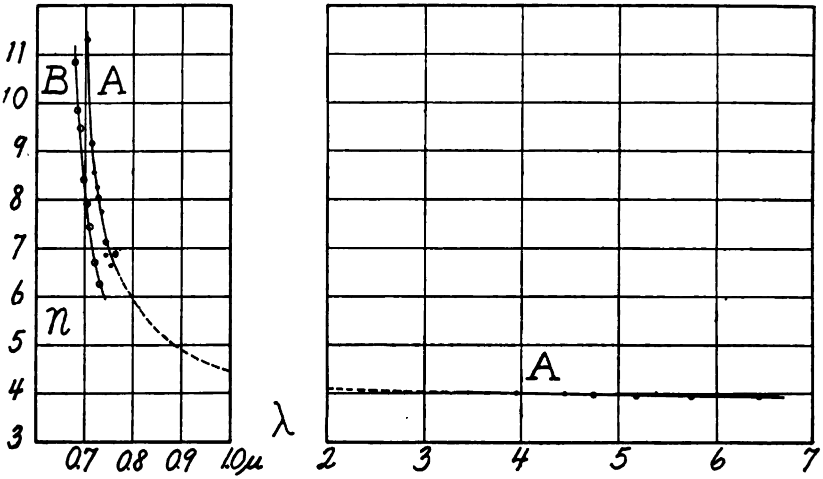

Fig. 9.

Curve A: Dispersion of molybdenite at ordinary temperature.
Curve B: Dispersion at temperature of liquid air.

The relation $n^2\chi = \sigma T$ may be tested for this substance. Calculating $\sigma = n^2\chi/T$ for several values of λ for which we have n, we find:

λ	n	$n\chi$	$\sigma = n^2\chi/T$
0.80 μ	6.00	3.9×10^{-4}	8.60×10^{11}
3.0	4.02	6.1 10^{-4}	2.45 10^{11}
4.0	4.0	7.5 10^{-4}	2.25 10^{11}
5.0	3.98	8.4 10^{-4}	2.00 10^{11}
6.0	3.94	9.7 10^{-4}	1.91 10^{11}
7.0	3.90	11.0 10^{-4}	1.85 10^{11}

A conductivity of 2×10^{11} electrostatic units is equal to a resistance of 4.5 ohms per c.c. Prof. A. Trowbridge, of Princeton, and Prof. G. W. Pierce, of Harvard, have made determinations of the specific resistance of this material which are, respectively, 3 ohms and 6 ohms per c.c.[1] at ordinary temperature (ca. 17° C.).

Through the courtesy of Professor Trowbridge the writer is enabled to communicate the following details regarding the optical properties of molybdenite at low temperatures:

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[1] Koenigsberger and Reichenheim (op. cit.) give for the resistance of molybdenite 3.06 ohms at 17° C. in the direction of the C-axis (the direction of light propagation in the present work). They also find that the conductivity increases rapidly with rising temperature. Pierce's data for the resistance of a molybdenite rectifier (Phys. Rev., 28, 1909, p. 151) exhibit this effect in a very striking manner.

A piece 4 or 5μ thick which was transparent down to 0.7020μ became transparent to 0.6660μ at the temperature of boiling liquid air ($-190°$ C.).[1]

A piece 4.1μ in thickness was kept immersed in liquid air and the interference bands in the visible region found with the aid of a concave grating to lie at the wave-lengths

0.7430μ
0.7320
0.7220
0.7130
0.7053
0.6977
0.6911
0.6854
0.6795
0.6750]
0.6720 .

The writer is unable to find data on the coefficient of expansion of molybdenite, but neglecting the effect of expansion on the thickness of the film, we compute, using formula 16, taking two bands at a time, the following values of the index:

λ	n
0.6757μ	14.8
0.6802	10.85
0.6853	9.86
0.6915	9.48
0.6982	8.40
0.7054	7.92
0.7136	7.44
0.7225	6.70
0.7325	6.24

This dispersion is plotted in Fig. 9, Curve *B*. The refractive index cannot possibly be independent of the temperature unless the coefficient of expansion is in the neighborhood of 0.001, which would be very high, say from 3 to 5 times as great as that of metals. The general facts set forth here agree very well with what Pulfrich found for glasses—namely, as the temperature fell, the ultra-violet absorption band moved toward the ultra-violet end of the spectrum, and the dispersion was decreased.

Other Sulphides.—Some other sulphides were ground into thin plates and tested qualitatively for transparency in the region $1\mu < \lambda < 6\mu$. It was difficult to produce thin layers of any accuracy and polish, but as the materials seemed to be opaque, no further attention was given them. The results are given in this table:

Material.	Thickness of Layer.	
Covellite, CuS,	about 0.2 mm.	Opaque, $\lambda < 6\mu$.
Chalcocite, Cu_2S,	about 0.5 mm.	
Galenite, PbS,	about 0.5 mm.	
Bismuthinite, Bi_2S_3,	about 0.2 mm.	Opaque in visible. Sample too small for infra-red work.

None of these specimens became transparent when cooled in liquid air.

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[1] Koenigsberger and Reichenheim established the fact that the transmission of total radiation by this substance was at 110° only 62 per cent. of the value at 40°. With regard to the

Koenigsberger and Reichenheim offer data on the reflecting power and transmission of pyrite, iron sulphide, and marcassite. They could not obtain similar films of galenite.

CONCLUSION.

While we have given approximate values for the refractive indices of stibnite and molybdenite, it is greatly to be desired that more accurate measures be made of these constants in the infra-red region. It is possible that very acute prisms of these materials could be filed out, and used in connection with a small spectrometer of short focal length. A prism of 1 or 2 mm. base would probably let through enough energy (where the energy spectrum is rich) to permit measurements by the method of minimum deviation.

A good determination of the electrical constants—conductivity and dielectric constant — is also necessary if much is to be done with these minerals.[1]

In molybdenite and stibnite we have two substances which in the near infra-red region have properties very much like those of ordinary transparent bodies in the visible—with the additional features of high refractive index and continued transparency for an indefinite distance with increasing wave-length. A two-term dispersion formula was applied to the dispersion curve of molybdenite, with the result that no solution for an absorption band in the distant infra-red could be obtained. Perhaps a method will be found for measuring the refractive index of the extraordinary ray in molybdenite, and determining the three refractive indices of stibnite. These results would be of great interest from a theoretical point of view.

A film of molybdenite a few microns thick offers possibilities with light of wave-length about 20μ for an investigation of the optical behavior of the film when twice its thickness is optically less than one wave-length.

The writer is under obligation to Prof. Augustus Trowbridge for suggesting this work, and for help and criticism throughout its progress. Prof. A. H. Phillips, of Princeton, has very kindly placed at the disposal of the writer his knowledge of mineralogy and crystallography and furnished an unusual crystal of sphalerite for this work.

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relation between conductivity and optical properties, it is well known that many oxides, sulphides, and other minerals which are poor conductors at ordinary temperatures become much more conducting when heated. For quartz and some other oxides, Doelter (op. cit.) found enormous decreases in resistance for specimens heated to 1300° C.

[1] Koenigsberger and Reichenheim give the conductivity of molybdenite (and its variation with temperature) in both crystallographic directions. They also give the conductivities of some of the other sulphides, but not of stibnite.

THE FLOW OF AIR THROUGH CAPILLARY TUBES.

By I. M. Rapp.

§ 1. The Problem.

A LARGE amount of work has been done on the flow of gases through capillary tubes, but most of it, especially that of recent years, has been done, not to secure an absolute value of the coefficient of viscosity, but rather to learn the law of temperature variation, the relative viscosities of gases, or of mixtures of gases, or finally, to find the point of "breakdown" of Poiseuille's law when the gas is driven through the tubes under very high or under very low pressure. With few exceptions, those later writers who have made absolute determinations of the viscosity coefficient give either very little data, or else such a wide range of variation in the separate trials, that it would be impossible, in trying to determine a probable value for the coefficient, to give, to each observer, a value proportionate to the accuracy of his work.

The chief difficulties encountered and the most probable causes of this great variation are found (1) in the smallness of the capillaries used, (2) in the irregularities of the bore, (3) in the method of calibration of the tube, (4) in the use of too large a driving pressure and (5) in the experimental difficulties such as the measurement of the volume and pressures and the holding of the latter constant.

Table I. gives a resumé of the best absolute determinations of the coefficient of viscosity of air which have been made by the capillary tube method. Nearly all of these observers have used tubes varying in radius from .05 mm. to .16 mm., while only one used a tube of radius greater than .22 mm.

A small radius means a decrease in the accuracy of its determination and since it enters in the fourth power in Poiseuille's law the error in the final result is increased in proportion. The development of the law is based on the assumption that the flow is in a tube of constant radius. This is an ideal condition which is seldom even approximated in tubes of small radius. In general, the bore of a capillary tube is conical, with minor variations from one end to the other. The solution of the equation for flow in a tube of varying conical bore has been neither made nor applied experimentally.

It has apparently been assumed by all of the earlier writers and by some of the later, that the R of Poiseuille's law can be determined from the length and mass of a column of mercury which will fill the tube. This assumption is erroneous. *It must always yield too high values of η, since it assumes that the resistance offered by the tube to the flow of fluid through it is inversely proportional to the cross-section instead of to the square of the cross-section.*

TABLE I.

Previous Absolute Determination of η, Reduced to 15° C.

	Author.	Reference.	Length of Capillary.	Radius of Capillary.	$\eta \times 10^7$
1	Grindley and Gibson	Proceedings of the Royal Society, Vol. 80, p. 114, 1908.	3298 cm.	.1585 cm.	1,783
2	Schultze	Annalen der Physik, Vol. 5, p. 140, 1901.	52.541	.0075717	1,811
3	Tanzler	Ber. d. D. Phy. Ges., Vol. 8, p. 222, 1906.	52.040	.007564	1,812
			52.4074	.00694717	
4	Fisher	Physical Review, Vol. 28, p. 73, 1909.	49.6	.00548	1,785
5	Rankine	Proceedings of the Royal Society, Vol. 83, p. 275, 1909.	49.06	.010230	1,799
6	Breitenbach	Annalen der Physik, Vol. 67, p. 803, 1899.	55.82	.010661	1,809
			95.43	.01381	1,804
7	Piwnikiewicz	Physikalische Zeitschrift, April, 1913.	36.55	.01772	1,796
8	Von Obermayer	Sitz. Ber. d. K. Ak. d. Wiss., Vol. 73, p. 433, 1876.	39.4	.0138	1,751
			50.2	.0196	
			36.0	.02241	
			39.7	.01525	
9	Schneebli	Arc. des Sci. Phys. et Nat. Genève, Vol. 14, p. 197, 1885.	39.95	.01236	1,871
			85.06	.01625	
			43.61	.01090	
10	O. E. Meyer	Die Kinetische Theorie der Gase, p. 189.	50 to 150	.0161 .00595 .00710	1,750 to 1,820
11	Warburg	Annalen der Physik, Vol. 159, p. 399, 1876.	74.9	.015076	1,840
			28.5	.009056	1,850
12	Puluj	Sitz. Ber. d. K. Ak. d. Wiss., Vol. 69, p. 287, 1874.	155.76	.0197353	1,863

Of the results shown in Table I., that of Grindley and Gibson is open to the least criticism. The remaining observers may be divided into two classes. First, No. 2 to No. 5, inclusive, who have made allowance for the irregularities in the bore of the tube, and second, No. 6 to No. 12, who have calibrated their tubes from the mass of a column of mercury which will fill it. The results of O. E. Meyer show no consistency, while those of Puluj and of Warburg are so out of line with the findings of all other experimenters as to be unquestionably in error by several per cent.; probably because of bends in the capillary and inequalities in the bore. The difference in the results of von Obermayer and of Schneebli is due to the one making allowance for the vapor pressure of the water used in securing the driving pressure while the other does not. If the data of both are treated the same way, identical values are given. The experimental work of Breitenbach and of Piwnikiewicz seems to have been done very carefully, but as they assume a uniform bore their results cannot be accepted as accurate absolute determinations. The variation in the result given by the observers in the first group is not due primarily, as is shown in § 3, to the theory in the methods of calibration, but rather to the experimental difficulties in calibrating tubes which are of the order of .0075 cm. radius and to the difficulties of maintaining the experimental conditions constant. In addition to this, the method which Rankine used to secure his driving pressure introduces errors which cannot be corrected.

The stream lines within the capillary are parallel to the wall when the driving pressure is small, but in the vessels at the ends of the tube they are radial. The development of Poiseuille's law does not take account of the energy in these radial lines. This suggests that there is a fall of pressure within the vessel at the ends of the tube. M. Brillouin and W. J. Fisher have independently developed expressions[1] for this correction which becomes appreciable in a tube 1 m. long and .13 mm. radius when the driving pressure is greater than 10 cm. of mercury. Fisher has applied his formula to his own data and finds the correction to be negligible. In Schultze's and Breitenbach's data the correction is .1 per cent. The data of Grindley and Gibson require no correction as they measured the pressures at points within the tube at such distances from the ends that the stream lines were parallel. The lengths and diameters of the tubes and the driving pressures used show that the correction should be made to the results of some of the other observers, but it is impossible to do so, as the data given are insufficient. Brillouin's correction has not been applied by any one.

The determinations of the coefficient of viscosity which have been made by other methods agree more closely with one another than with those secured by the use of the capillary tube. Further, the accuracy of the value of the elementary electric charge,[2] as determined by the method developed by Professor R. A. Millikan, depends on the absolute value of the coefficient of viscosity. Since in that method η is the factor whose value is most in doubt, it became necessary that it should be redetermined with the greatest accuracy possible. Hence the following investigation was undertaken with a view of eliminating, as far as possible, the sources of error incidental to the capillary tube method and of seeing whether or not it is capable of yielding a value in agreement with that found by other methods. The distinct features of the research are:

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[1] See § 5.

[2] Millikan, Phys. Rev., Vol. 32, p. 349, 1911.

1. The selection of very uniform tubes.
2. The use of a considerable number of tubes of quite different dimensions.
3. The accurate calibration of these tubes.
4. The use of small but constant and accurately measurable driving pressures.
5. The experimental study of the end correction.

§ 2. SELECTION OF TUBES.

The tubes used, which were made of Jena glass, were selected for their circularity of cross-section and uniformity of bore so that the first two probable sources of error mentioned above might be made as small as possible. Those whose cross-section showed ellipticity when viewed under a twenty-power microscope were immediately cast aside and none were accepted unless the axes were shown by micrometer measurements to be approximately the same. The tubes which were broken in a later part of the research showed the same circular cross-section. The uniformity of bore was tested and only those tubes which showed neither sharp and abrupt changes nor large variations in their diameter were finally chosen. The tubes were cleaned by forcing through them solutions of potassium bichromate in sulphuric acid, potassium hydroxide, nitric acid and distilled water. During the process of cleaning they were kept at the temperature of steam by surrounding them with a jacket through which a current of steam was continually passing. One end of the tube was immersed in the cleansing liquid while the other extended into a flask which could be exhausted by means of an air pump. After the nitric acid had been washed out with the distilled water, absolute alcohol and dry air were driven through in order to remove the moisture. The bore was carefully examined for particles of dirt and the process of cleansing repeated until the tube was clear. As a further check it was recleaned after a number of viscosity determinations had been made. The fact that the same results were secured after recleaning was taken as proof that the tube was clean.

§ 3. Calibration of Tubes.

There are three methods by which the R of Poiseuille's law may be determined. The first is by the simple method of measuring the length and mass of a column of mercury which will fill the tube. The second was developed by Schultze[1] and consists experimentally in finding the value of L/R^4 from the volume and length of a short column of mercury at positions every two centimeters along the tube. The calibrating factor is computed from the equations:

$$\frac{L}{R^4}=\sum_0^L\frac{l}{r^4}=\frac{\pi^2}{v^2}\sum_0^L\lambda^2 l \tag{1}$$

and

$$v=\frac{U}{\sum\limits_{l_1}^{l_2}\frac{l}{\lambda}}, \tag{2}$$

in which λ, r and v are respectively the length, radius and volume of the calibrating thread, l is the length of a portion of the tube over which the radius is assumed to be constant and U is the entire volume of the tube between the points l_1 and l_2. The third method was proposed by Fisher[2] and experimentally is identical with Schultze's. But his development is different, as he assumes that the radius is constant over an infinitesimal length, dl, of the tube and that the square of the fall in pressure over this length is dp^2. From these considerations he shows that

$$\frac{L}{R^4}=\frac{\pi^2}{U^2}\int_0 \lambda^2 dl\left[\int_{l_1}^{l_2}\frac{dl}{\lambda}\right]^2. \tag{3}$$

The values of the integrals are computed from the areas of the two curves formed by plotting λ^2 and $1/\lambda$ with l. Although developed by different methods, the two calibration equations are theoretically identical if we assume that the radius is constant over the same length of tube. In equations (1) and (2) l thus becomes dl and the summations become integrals. The combination of equations (1) and (2) is then identical with equation (3).

The tubes used in the absolute determination of the coefficient of viscosity were calibrated by Fisher's method. A check on the accuracy on his formula for the determination of the volume of the calibrating thread was had in the calibration of tube No. 4, by comparing the volume of the thread, obtained from its mass and density, with that computed by the formula

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[1] Schultze, Annalen der Physik, Vol. 5, p. 140, 1901.

[2] Fisher, Phys. Rev., Vol. 28, p. 73, 1909.

$$v = \frac{U}{\int_{l_1}^{l_2} \frac{dl}{\lambda}}.$$

A difference of .2 per cent. between the two values was found. As this was less than the estimated error in the weight, Fisher's formula was considered to give the true value of v.

TABLE II.

The Radii of the Tubes Computed by the Different Methods of Calibration.

Tube No.	By Mass of Column of Hg.	By Schultze's Calibration.	By Fisher's Calibration.	Per Cent. Change in η by the Use of R of Column No. 2.
1	.023356 cm.		.023352 cm.	+0.01
2	.0129288		.0129214	+0.23
3	.0057800	.0057586 cm.	.0057581	+1.5
4*a*	.0251106	.025012	.025012	+1.7
4*e*	.0251106		.0251110	−0.01
5	.017119		.017114	+0.1
6	.0056551		.0056419	+1.0

In Table II. are given the values of the radii computed by the different methods. Only two tubes were calibrated by Schultze's formula. Both results were identical with those given by Fisher's method. If column No. 2 is compared with column No. 4, it is seen that the calibration by the use of the mass of the total column of mercury yields in every case too high a value of R and hence too high a value of η, as it should in view of the theoretical considerations mentioned above. The last column shows how much too high even with the use of these very uniform tubes the value of η would have been if this method of calibration had been used.

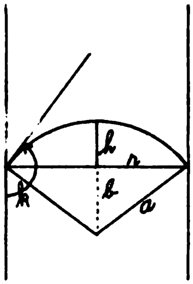

Fig. 1.

Both Schultze and Fisher in their methods of calibration consider that λ is obtained by adding one half the height of the meniscus to the apparent length of the mercury thread. This is true if the radius of the tube is small and consequently the height of the meniscus small, but will not be true if the tube is large.

The method of allowing for the meniscus in the larger tubes which were calibrated for this problem was as follows:

In Fig. 1, let r be the radius of the tube,
a be the radius of the spherical segment,
h be the height of the meniscus,

A be the area of cross-section of the tube,
V be the volume of the segment,
K be the angle of contact between glass and mercury,
$K = 141° 8'$.

From the figure

$$b = a - h = a \cos 51° 8',$$
$$r = a \sin 51° 8',$$
$$A = \pi r^2 = \pi a^2 \sin 51° 8',$$
$$a = h + b = h + a \cos 51° 8',$$
$$a = \frac{h}{1 - \cos 51° 8'},$$
$$V = \pi\left(\frac{2a^3}{3} - a^2 b + \frac{b^3}{3}\right).$$

The mean height of the meniscus, V/A, then becomes, when the substitutions are made, 0.53 h. A variation of several degrees in the angle of contact does not change the result more than one per cent., a variation which is negligible and which would allow for the assumption in the figure that the wall of the tube is parallel to its axis. The thread of mercury may be considered to be the frustum of a right circular cone capped by portions of spheres as described above.

If r is the radius at the middle point, Δr the difference between r and the radii of the ends, v the total volume of the thread and λ_1 the length of the thread between the menisci,

$$v = \pi\lambda_1\left(r^2 + \frac{\overline{\Delta r^2}}{3}\right) + (V_1 + V_2).$$

Let λ be the length of a right circular cylinder of radius r and volume v.

$$v = \pi r^2 \lambda = A\lambda.$$

The solution of these two equations gives

$$\lambda = \lambda_1\left(1 + \frac{\overline{\Delta r^2}}{3r^2}\right) + \left(\frac{V_1 + V_2}{A}\right).$$

$\overline{\Delta r^2}/3r^2$ is an exceedingly small fraction.

A difference of not less than 6 per cent. in the radii of the bases of the frustum is necessary to cause a change in λ which can be determined by the dividing engine. Since the actual variation in the tubes did not even approach this value, the thread of mercury can be considered as a cylinder and the radius of the tube, over this length, a constant. The expression $(V_1 + V_2)/A$ then becomes 0.53 $(h_1 + h_2)$ and

$$\lambda = \lambda_1 + .53\,(h_1 + h_2).$$

With the tubes of smaller radius, where h is small compared to λ no appreciable error is made in taking $\lambda = \lambda_1 + \frac{1}{2}(h_1 + h_2)$.

The theoretical value of V/A as determined above only approximates the true value of h. An exact mathematical expression cannot be obtained, as h is not the simple function of K which has been assumed. It was noticed in calibrating all of the tubes, that, in general, the forward meniscus was larger than the rear one. This seemed to be independent of the direction in which the mercury was moved past a given point and therefore was caused by friction between the wall of the tube and the mercury.

The calibration measurements were made on a Société Genevoise dividing engine. A comparison of the screw with the standard decimeter scale at the Ryerson Physical Laboratory showed only deviations which were well within the limits of experimental error.

A column, about 1.5 cm. long, of triple distilled mercury, which showed no surface impurities, was used as the calibrating thread. The mercury was pushed from one end of the tube to the other, care being taken to see that each new position slightly overlapped a part of the previously measured portion. This insured that all of the tube was covered in the calibration. The column was then forced back and forth a second and third time and its length measured in positions at such distances apart that finally every portion of the tube was covered a second time.

All weighings were made on a chemical balance with the use of a set of Sartorius double check weights accurate to .01 mg. The ordinary precautions for accurate weighing, as double weighing, reduction to weight in vacuo, etc., were observed. It was estimated that the error made in weighing the mercury column for tube No. 2, the smallest tube, was not more than .1 mg. This is an accuracy of 1 part in 7,000 and affects the value of η only .03 per cent. The errors made in the weights of the mercury column for the other tubes were of the same order.

§ 4. THE METHOD.

The simple form of Poiseuille's law is:

$$\eta = \frac{\pi R^4(p_1^2 - p_2^2)t}{16VLp_2}.$$

If we substitute in this equation the value of R^4/L obtained from (3) and then, for brevity, use the single letter K to denote

$$K=\frac{U^2\rho g}{16\pi\int_0^L\lambda^2dl\left[\int_{l_1}^{l_2}\frac{dl}{\lambda}\right]^2},\tag{4}$$

ρ being the density of mercury at 0° C. and g the acceleration of gravity, it becomes

$$\eta=\frac{K(p_1-p_2)(p_1+p_2)t}{p_2V}.\tag{5}$$

K, defined by equation (4), is a constant whose value depends on the dimensions of the capillary used. The values of this constant for each tube are given in the last column of Table III. The calibration of the tubes was made at temperatures between 23° C. and 24° C. and reduced to 26° C. by the formulæ[1] used by Fisher in the calibration of his tubes.

Table III.

The Dimensions of the Tubes and the Values of Log K.

Tube No.	Length in Cm.	Diameter in Cm.	Log K.
1	99.6062	.046704	$\bar{6}.892782$
2	99.5837	.025843	$\bar{7}.865840$
4*a*	87.4652	.050024	$\bar{5}.069050$
4*b*	77.2469	.050086	$\bar{5}.124663$
4*c*	67.1552	.050156	$\bar{5}.187887$
4*d*	56.9004	.050225	$\bar{5}.262221$
4*e*	51.9656	.050222	$\bar{5}.301507$
5	76.3662	.034228	$\bar{6}.468550$

Equation (5) when corrected for slip becomes

$$\eta=K\frac{(p_1-p_2)(p_1+p_2)t}{p_2V}\left(1+4\frac{\xi}{R}\right).\tag{6}$$

The coefficient of slip, ξ, used, is .000083 cm. at a pressure of 76 cm. This is the result obtained by Millikan in his work on the elementary electric charge and is close to that obtained by Warburg[2] by the flow of air through capillary tubes.

If in equation (6), p_1 is the barometric pressure and p_1 and p_2 are large in comparison to their difference, the accuracy of the experiment depends mostly on the measurement of (p_1-p_2). The apparatus was planned to secure accuracy in the volume of air transpired and both constancy and accuracy in the driving pressure. Transformer oil, in preference to mercury, was used in the manometer and in the apparatus to secure the difference in pressure, because, it being less dense, lower driving pressures could be read more accurately and the manometer variations were made more noticeable and were more easily controlled. Obermayer and Schneebli used water to secure their pressure difference. Their results show that evaporation introduced an error. The transformer oil having an inappreciable vapor tension eliminated it.

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[1] Fisher, Phys. Rev., Vol. 28, p. 73, 1909.

[2] Warburg, Pogg. Annalen der Physik., Vol. 159, p. 399, 1876.

The air used in the experiment was taken from the pressure system in the laboratory and made dust-free and dry by passing it in succession through sulphuric acid, calcium chloride, phosphorous pentoxide and glass wool. Atmospheric pressure at the inlet end of the capillary was secured by the trap *A* (see Fig. 2). This was arranged so that the air which entered from the drying system could pass either into the coil *C* or escape into the atmosphere through a carboy *B*. A layer of phosphorous pentoxide was placed in the latter to provide against the diffusion of moisture from *B* into *A*. The pressure in the trap thus automatically

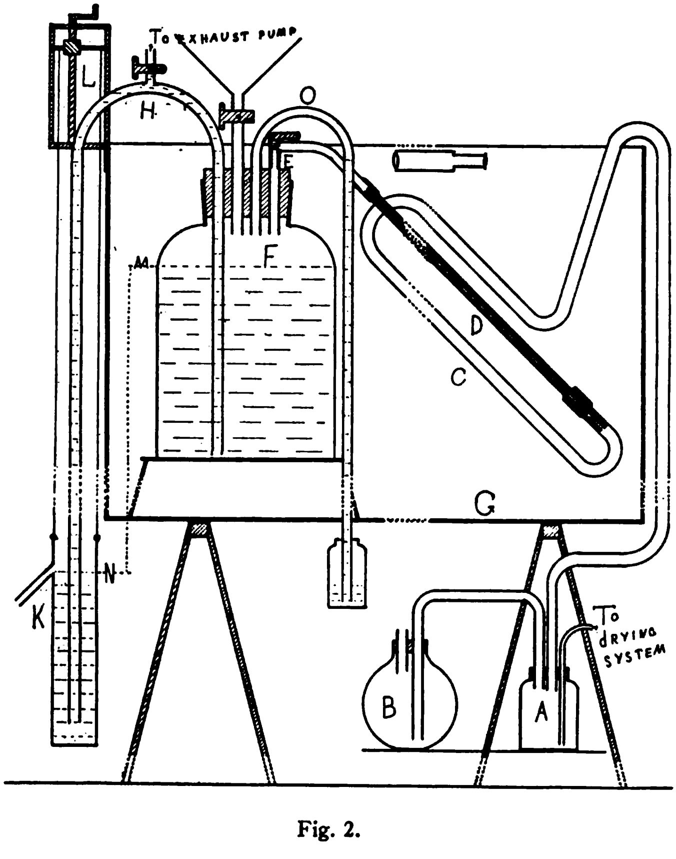

Fig. 2.

adjusted itself to that of the atmosphere. The coil *C*, used to insure a constant temperature of the air, was placed between the trap and the capillary *D*. The tubing used in the trap and in the coil *C* was of such size that actual tests showed no fall of pressure along it. From the capillary, the air passed through the stopcock, *E*, into the apparatus for securing the reduction of pressure and the measurement of the volume of air transpired. The coil *C*, the capillary *D*, and the apparatus *F* for measuring volume were submerged in a tank of water *G*. A series of incandescent lamps submerged in the water and lighted automatically by means of a mercury thermostat, kept the temperature at 26° C. with a possible error of .02° C. and with a variation, during the taking of a set of readings, of not more than .003° C. The temperature was measured on a Baudin thermometer of which the tables for reduction to the temperature on the hydrogen thermometer were known. A Beckmann thermometer, graduated in .01° C., was used to determine the constancy of the bath and was compared with the Baudin thermometer at frequent intervals.

The driving pressure was obtained by means of a tube *H*, which led from the bottom of the reservoir *F*, and whose lower end extended into a bucket *K*, which was suspended from a micrometer *L*. When the three were filled with the oil, the air in *F* was under a pressure lower than atmospheric pressure by the weight of a column of oil whose height is the distance *MN* between the surfaces in the reservoir and in the bucket. This height, which is the driving pressure, was not measured directly but by means of the manometer *O*. As the capillary admitted air to the reservoir the pressure in it was kept constant by lowering the bucket with the micrometer at such a rate that the upper surface of the liquid in the manometer was kept stationary. The motion of the image of a lamp, seen in the meniscus, when viewed through a twenty-power telescope, made it easy to control the variation in pressure. The error in maintaining the manometer height constant was absolutely negligible, as the variation in position of the spot of light was not more than .5 mm. from the cross-hairs in the telescope. A variation of .5 mm. in 100 cm., the lowest approximate manometer reading used, shows the accuracy with which the driving pressure was kept constant.

The manometer and outlet tubes were exposed to the room, which could not be kept at a constant temperature. This caused changes in the driving pressure and in the mass of oil in the outlet tube and bucket. The temperature of the manometer was taken as the mean of the readings of two or more thermometers suspended at different points beside it. An error of 1° C. in the temperature of the manometer would cause an error in the result of nearly .1 per cent.

When air enters the reservoir through the capillary, oil is displaced. The volume which flows out of the bucket in a given time is determined from the mass and density. This, when the few slight corrections which follow are made, is the volume of air, V, which has passed through the capillary during the measured time.

A change in the barometric pressure during a test causes a change in the initial volume of air in the reservoir. To make this correction, the approximate volume and the pressure both at the beginning and at the end were determined. The application of Boyle's law gave the correction.

The error caused by the change in temperature in the outlet tube and bucket was estimated from the temperatures and volumes of the oil in the bucket and outlet tube at the beginning and at the end of the observation. The correction for temperature, in a few trials, reached .5 per cent., but was seldom more than .2 per cent.

During the time of observation, the bucket K was lowered. Since the outlet tube extended beneath the surface of the oil, a volume of oil was added equal to a cylinder whose cross-section is that of the tube and whose length is the distance the bucket was moved. Finally a correction due to the vaporization of the oil and to leakage was necessary in the case of tube No. 2 when the driving pressure was greater than 24 cm. of mercury. Frequent tests at other pressures and with other tubes showed that a correction was unnecessary.

Weighings of the oil, in the determination of the volume of air, were made to the .1 g. A set of accurate analytical weights was used and the correction made for weight in vacuo. The accuracy of the balance was such that double weighing was unnecessary.

A comparison of equation (6) with the description of the apparatus shows that the measurement of $(p_1 - p_2)$, p_2 and V depend on the density of the transformer oil used. Thus, since it enters directly in the determination of two of the quantities and indirectly into the third, the density of the oil is actually a factor in the equation as if it were raised to approximately the five-halves power. This necessitated an accurate determination of its density. At least two different samples of each lot of the oil used were tested at several temperatures between 12° C. and 26° C. The line drawn through the mean position of all of the determinations on a given lot of oil showed a maximum variation of the points from the line of 3 parts in 8,400. This would make a probable error in the value of η of less than .1 per cent.

The times were measured by a stop-watch which was compared at frequent intervals with the standard clock in the Ryerson Laboratory. These comparisons showed that the personal error of manipulation was not more than .4 sec. on any one reading. Errors of adjustment were allowed for and finally when the watch was more carefully adjusted they were negligible. Just before the taking of a set of readings it was wound and during the observation of time was kept in a horizontal position.

The atmospheric pressure was read on a Fortin barometer having a vernier reading to the thousandths of a centimeter. A comparison with the standard barometer at the U. S. Weather Bureau at Chicago was made when work on the problem was begun. The slight difference in the readings was allowed for in the data.

§ 5. The Correction for the Fall of Pressure at the Ends of the Tube.

Osborne Reynolds[1] has made a study of the flow of water through capillary tubes and finds that Poiseuille's law breaks down and the flow becomes turbulent when

$$1{,}900 < \frac{2U_m\rho R}{\eta} < 2{,}000.$$

ρ is the density and U_m the mean velocity of the liquid in the tube. W. Ruckes[2] has found that this law is applicable to the flow of air through capillary tubes of various lengths and diameters. It will appear from the results which follow that, in my data, there are appreciable departures from Poiseuille's law. If, then, Reynolds' law holds, the velocity of the air in those tubes should be above the critical velocity. The actual value of the velocity of the gas in tube $4e$, at the greatest driving pressure used, was 1,100 cm. per second, while the critical velocity, or the velocity at which, computed by Reynolds' law, turbulent motion sets in and Poiseuille's law breaks down, should be 6,800 cm., that is, six times as large. This does not prove that, when applied to gases, Reynolds' law is in error as to the point when turbulent motion sets in, but rather it demonstrates that there are departures from Poiseuille's law which take place before turbulent motion begins. These departures are due to the energy in the stream lines at the ends of the tubes.

A modification of Poiseuille's law, which corrects for these end effects has been developed by M. Brillouin.[3] He considers that the flow from the one vessel to the other causes a fall in pressure along the stream lines which are outside of the tube. Some kinetic energy is therefore acquired by the moving fluid and some work is done which is not taken into account in the ordinary development of the law. In applying this idea to a gas, he states that "This kinetic energy is that of the emergent jet." From this assumption a modified form of Poiseuille's law is shown to be

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[1] Osborne Reynolds, Scientific Papers, Vol. II., pp. 51 and 535.

[2] Ruckes, Annalen der Physik, Vol. 25, p. 983, 1908.

[3] Brillouin, Lecons sur la Viscosité des Liquides et des Gas, Vol. 1, p. 133; Vol. 2, p. 37.

$$p_1^2 - p_2^2 = \frac{p}{\rho}\left[\frac{16\eta LM}{\pi R^4\left(1 + \frac{4\xi}{R}\right)} + \frac{2M^2}{\pi^2 R^4}\right].$$

M is the mass of gas transpired per unit of time and ρ, the density at the pressure $\frac{1}{2}(p_1 + p_2)$. The other letters have the same significance as elsewhere in this paper. This formula shows that the correction due to the drop in pressure bears the same ratio to the coefficient of viscosity as M bears to $8\pi\eta L$.

Fisher has criticized[1] this in the following words: "The velocity of the emergent jet is not due wholly, as for a liquid, to the initial pressure; a good share of it is due to work done inside the tube itself, especially if the expansion is isothermal and heat energy has been supplied all along the tube to keep up the temperature." Reasoning from this and from O. E. Meyers' integration of the equations of flow of gases through capillary tubes he develops[2] the following formula for the correction to the entrance pressure:

$$R'T \log_e \frac{p_1}{p_1'} = -\frac{1}{384}\left[\frac{p_1^2 - p_2^2}{\eta p_1 L}\right]^2 [R^4 + 12\xi^2 R^2 + 6\xi R^3].$$

R' is the constant of the gas equation, T, the temperature of the gas on the absolute scale, p_1 the pressure to be used in Poiseuille's law and p_1' the manometer pressure measured in the vessel at the end of the tube. A similar formula with the subscripts 2 gives the correction to the exit end.

My own observations, as will appear in the following tables, have been reduced by means of both Brillouin's and Fisher's formula.

§ 6. THE DATA.

The determination of the coefficient was made at three driving pressures. Table IV. includes the complete data of one trial for each of the driving pressures which were used with each tube. On the average, about 10 trials were made at a driving pressure with each tube. The values of $\eta \times 10^7$ in the last column are computed from the data in the corresponding lines and are not corrected for slip or for end effects.

Table V. gives the mean values of η for all of the trials made with each tube at the given driving pressures when the corrections for slip and for end effects have been made. The number of trials made with a tube at the given driving pressure is shown in the last column. The probable error, P, is determined from the formula

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[1] Fisher, PHYS. REV., Vol. 29, p. 152, 1909.

[2] PHYS. REV., Vol. 32, p. 216, 1911.

$$P = \pm 0.67 \sqrt{\frac{\Sigma d^2}{n(n-1)}},$$

in which Σd^2 represents the sum of the squares of the differences between the separate trials and the mean of the n trials.

Table IV.

Data for η. Temperature, 26° C.

Tube No.	p_1+p_2 in Cm. of Hg.	p_2 in Cm. of Hg.	p_1-p_2 in Cm. of Hg.	V in Cm.^{3}	t in Sec.	$\eta \times 10^7$ by Equation (5).
1	142.459	67.946	6.674	817.8	1383.8	1838.7
	138.915	64.357	10.227	567.9	605.7	39.3
2	142.828	68.254	6.320	381.6	7203.8	33.1
	138.699	64.233	10.233	400.2	4518.1	31.7
	124.605	50.045	24.515	519.8	2127.4	36.1
4*a*	142.530	68.018	6.504	602.9	693.6	42.3
	139.497	64.601	10.295	605.2	428.4	44.5
4*b*	142.234	67.907	6.420	588.9	606.0	44.0
	138.425	64.128	10.169	582.7	367.4	44.2
4*c*	142.407	68.001	6.405	477.6	425.3	41.2
	138.978	64.408	10.162	669.7	365.4	44.1
4*d*	141.867	67.800	6.267	1132.3	872.4	48.0
	138.487	64.130	10.227	664.9	306.0	59.1
4*e*	143.057	68.375	6.307	951.0	666.2	51.2
	138.751	64.273	10.205	663.4	279.0	56.7
5	138.786	64.308	10.170	405.5	1151.1	32.6

Table V.

Mean Values of η at the Different Driving Pressures.

Tube No.	(p_1-p_2) Cm. of Hg. (Approx. Value).	$\eta \times 10^7$ by Equation (5).	$\eta \times 10^7$ Corrected for Slip by Equation (6).	$\eta \times 10^7$ Corrected for Slip and for End Effects.		P, Probable Error $\times 10^7$.	n, Number of Trials.
				By Brillouin's Formula.	By Fisher's Formula.		
1	6 +	1,838.0	1,841.7	1,839.2	1,839.2	±0.5	12
	10 +	1,839.0	1,842.1	1,838.3	1,837.5	±0.3	24
2	6 +	1,833.0	1,838.1	1,837.9	1,837.5	±0.1	2
	10 +	1,831.2	1,836.5	1,836.1	1,836.5	±1.0	4
	24 +	1,834.7	1,840.5	1,839.7	1,839.2	±0.1	3
4*a*	6 +	1,842.1	1,844.7	1,839.6	1,836.6	±0.3	12
	10 +	1,844.4	1,847.1	1,840.1	1,838.4	±0.2	21
4*b*	6 +	1,844.3	1,846.9	1,841.6	1,839.3	±0.2	6
	10 +	1,844.4	1,847.1	1,839.9	1,837.1	±0.2	9
5	10 +	1,832.8	1,836.8	1,834.8	1,834.9	±0.5	16

Table VI. is a condensation of Table V. and gives, in column No. 2, the mean value for each tube when the same weight is given to each trial. In this column the correction has been made for slip. Column No. 3 gives the results in column No. 2 when corrected for end effects by Brillouin's formula and column No. 4 the same results corrected by Fisher's formula.

TABLE VI.

Mean Values of $\eta \times 10^7$ *for Each Tube.*

Tube No.	$\eta \times 10^7$ Corrected for Slip by Equation (6).	$\eta \times 10^7$ Corrected for Slip and for End Effects.	
		By Brillouin's Formula.	By Fisher's Formula.
1	1,842.0	1,838.6	1,838.1
2	1,838.3	1,837.7	1,837.6
4*a* and 4*b*	1,846.5	1,840.1	1,837.8
5	1,836.8	1,834.8	1,834.9
Mean...	1,840.3	1,837.8	1,837.1

Table VII. shows the final mean values given by three more tubes, 4*c*, 4*d* and 4*e*, which were obtained by cutting off tube No. 4. The corrections for slip and for end effects have been made.

TABLE VII.

Mean Values of $\eta \times 10^7$ *for Tubes 4c, 4d and 4e.*

Tube No.	Length of Tube in Cm.	$p_1 - p_2$ in Cm. of Hg. (Approx. Value).	$\eta \times 10^7$ by Equation (5).	$\eta \times 10^7$ Corrected for Slip by Equation (6).	$\eta \times 10^7$ Corrected for Slip and for End Effects by		No. of Trials.
					Brillouin's Formula.	Fisher's Formula.	
4*c*	67.16	6 +	1,840.6	1,843.2	1,835.8	1,834.9	4
		10 +	1,844.8	1,847.5	1,838.2	1,832.2	2
4*d*	56.90	6 +	1,850.1	1,852.7	1,842.8	1,839.7	3
		10 +	1,859.5	1,862.2	1,845.9	1,841.7	4
4*e*	51.97	6 +	1,849.5	1,852.1	1,840.0	1,835.9	2
		10 +	1,856.7	1,859.4	1,839.8	1,835.3	4
			Mean...............		1,840.3	1,836.6	

§ 7. A DISCUSSION OF THE DATA.

An analysis of Table V. shows that when the correction for slip alone has been made, different values of η are given by different driving pressures and the same tube, or by different tubes and the same driving pressure. When, however, the corrections are made either by Brillouin's or by Fisher's formula the values are all brought into fairly good agreement. The variations due to a change in the driving pressure alone are so small, that, from this table, no inference can be drawn as to which method of correction is the better.

But if we compare the values for each tube as found in Table VI., where, with a given tube, each trial receives the same weight, a different result appears. Fisher's formula gives values for three of the tubes which are identical for four figures while Brillouin's correction permits a variation in the fourth place. Too much weight, however, must not be given to this fact, since, if the accuracy of the experiment were what these three results suggest, the values of η obtained at the different pressures for a given tube (see Table V.) would be just as close as the values in Table VI. As this is not the case, Fisher's formula cannot be said to be demonstrated to be better than the other. Table VII., however, contains data favorable to Fisher's formula.

Tube No. 4 was the largest one used and, as is seen from Table V., requires the largest end corrections. To obtain an empirical formula for this correction the tube was shortened by 5 cm. and 10 cm. at a time and the values of η observed and computed.

The original tube, 4*a*, and the second length, 4*b*, gave practically identical results (see Table V.) but the third length, 4*c*, gave values of η which began to differ appreciably with the change in driving pressure (see Table VII.). A comparison of these values at the different pressures for the same length of tube, when corrected for end effects, shows that Fisher's formula makes the variation in the results less than does Brillouin's. Further, the mean of all of the trials is nearer the mean value, given in Table VI., than is the corresponding value obtained by applying Brillouin's expression.

A further careful study of the data in Tables V. and VII. shows that the correction for the end effects is a direct function of the driving pressure and of the fourth power of the radius and an inverse function of the length. This may be expressed by the equation

$$\eta = \eta' \left[1 + \frac{A(p_1 - p_2)R^4}{L} \right]$$

if the terms of order higher than the first are neglected. In this equation A is a constant and η' is the coefficient when corrected for slip. The value of A, determined from the data of tube No. 4, is

$$A = -1.25(10^5).$$

An empirical formula, which will correct the error in η' due to the end effects, is therefore given by

$$\eta = \eta_1'\left[1 - 1.25(10^5)\frac{R^4(p_1 - p_2)}{Ll}\right].$$

This equation is equivalent to Fisher's correction, as it gives values which are identical within the limit of experimental error with those obtained by his theoretical formula.

The results given in Table VII. are not of such accuracy that one may say that either the empirical or Fisher's formula completely expresses the end effects. The values of η should increase consistently with a decrease in the length of the tube. This they fail to do. The empirical determination of the proper correction for the fall in pressure at the ends of the tube would therefore necessitate a series of more accurate experiments than those on which I have based my absolute determination of η.

§ 8. THE RESULT.

The mean values of η when the different corrections have been made are given in Table VI. Only the data obtained by the use of those tubes in which the end correction is small, have been used for the absolute value of the coefficient. The mean value given by these tubes, when the correction for slip is made, is $1840.3(10^{-7})$. When the correction both for slip and for the end effects are made by Brillouin's formula, it is $1837.8(10^{-7})$ and when made by Fisher's formula, $1837.1(10^{-7})$. The end effects are therefore small but not negligible. Since the two methods of correction give values which differ by but one fortieth of one per cent. their mean is taken as the result obtained in the investigation. This gives an absolute value of $1837.5(10^7)$ g./cm. sec. for the coefficient of viscosity of dry air at 26° C.

The uncertainty in this value of η may be estimated from the following considerations. The maximum variation of a single trial from the mean of the values for a given tube at a given driving pressure is .1 per cent. for the most consistent series and .4 per cent. for the least consistent. The probable error in a given series, as is seen in Table V., is in no case greater than .06 per cent. Such a series of course involves systematic errors which, however, disappear in the mean result found in Table VI., since this table contains completely independent determinations on different tubes. The probable error, in the mean of Table VI., when computed in the usual way, is .04 per cent. This assumes that the correction for the end effects has been properly made. In order to make allowance for possible uncertainties arising from the method of making this correction we may take the total uncertainty in the final value as about .1 per cent. The results found by other observers who have not made allowance for the variation in the radius are higher than this, as they should be.

The value obtained by Grindley and Gibson is identical, while that given by Fisher differs only by about .1 per cent. My result agrees within .1 per cent. with the mean of the very accurate determinations made by Gilchrist,[1] by the use of a constant deflection method, by Hogg,[2] from the damping of oscillating cylinders, and by Tomlinson,[3] by the damping of a vibrating pendulum.[4] In fact the only careful determinations by any method which do not agree with this were made at the University of Halle by Schultze, by Tanzler and by others using Schultze's apparatus. The reason for their high values is most probably found in the use of the exceedingly small tubes, which makes the determination of the radius difficult and very uncertain.

§ 9. THE SUMMARY.

In the above study of "The Flow of Air Through Capillary Tubes" a number of tubes of different diameters and of very uniform bore were selected and carefully calibrated. With these tubes, both an experimental study of the fall in pressure at the ends and a determination of the absolute value of the coefficient of viscosity of dry air were made.

The study of the end effects leads to the following conclusions:

I. The method of allowing for the end effects, developed by M. Brillouin, holds only for very small corrections.

II. The method developed by Fisher expresses the result better for the corrections within the range of this investigation.

III. The empirical formula,

$$\eta = \eta' \left[1 - 1.25(10^5) \frac{R^4(p_1 - p_2)}{L} \right],$$

which is deduced from the data, gives results which are equivalent to those obtained by Fisher's method.

The absolute value of the coefficient of viscosity of dry air obtained in this investigation at 26° C., when the corrections for slip and for end effects have been made, is $1837.5(10^7)$ g./cm. sec. with an estimated experimental error of .1 per cent.

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[1] Gilchrist, PHYS. REV., Series II., Vol. I., p. 124, 1913.

[2] Hogg, Proceedings of the American Academy, Vol. 40, p. 611, 1905.

[3] Tomlinson, Philosophical Transactions of the Royal Society, Vol. 177, p. 767, 1886.

[4] A summary of these determinations is given by R. A. Millikan, "Ueber den warscheinlichsten Wert des Reibungskoeffizienten der Luft," Annalen der Physik, Vol. 41, p. 759, 1913.

In conclusion, I take this opportunity of thanking those who have very willingly assisted during the progress of the research. I wish, especially, to acknowledge the encouragement and the timely suggestions which Prof. R. A. Millikan has given. The investigation was undertaken at his suggestion and was carried to completion under his supervision.

Ryerson Laboratory,
The University of Chicago,
August, 1913.

THE LONGITUDINAL THERMOMAGNETIC POTENTIAL-DIFFERENCE.

By Alpheus W. Smith.

IF a plate in which there is a longitudinal flow of heat is brought into a transverse magnetic field so that the lines of force are perpendicular to the plane of the plate, it is found that there is a difference of potential set up between any two points at a given distance apart along the plate. This difference of potential is superposed on the thermoelectromotive force which exists in the plate and may serve to increase or to decrease it. Following the usual practice this effect will be considered positive when the potential-gradient established by the magnetic action is in the same direction as the temperature-gradient along the plate. The coefficient of this effect is given by the equation,

$$e = LH\frac{\partial t}{\partial x}l$$

or approximately

$$L = \frac{e}{H(t_1 - t_2)},$$

where e is the difference of potential in absolute units called forth by the magnetic action; H is the magnetic field in absolute units; and $t_1 - t_2$ is the difference of temperature between the two points on the plate at which the lead wires to the galvanometer are soldered, and l the distance between these points.

Zahn[1] has made observations on the way in which this effect in bismuth depends on the temperature. For a magnetic field of 6,290 absolute units he found L to be 0.134 at 28.7° C. and 0.111 at 24.1° C. From these observations he concludes that this effect in bismuth increases with rising temperature. It seemed desirable to study more fully the influence of temperature on this effect in bismuth.

The bismuth plates to be investigated were cast by pouring the molten bismuth into a lavite mould. These plates were about 3 cm. long, 1.4 cm. wide and 0.2 cm. thick. The apparatus for producing the temperature-gradient in the plates was essentially the same as that used by the author[2] in the study of the transverse thermomagnetic effect in nickel

[1] Ann. der Phys., 14, p. 914 (1904).

[2] Phys. Rev., 33, p. 295 (1911).

and cobalt at different temperatures. For the details of the apparatus reference is made to Fig. 1 of that paper. In the present experiments, however, slots were cut in the ends of the rods which were opposite to each other and into these slots the plates to be investigated were inserted. The plates were then clamped to the copper rods by means of screws. To each end of the plate on its longitudinal axis was clamped a copper-advance thermal junction by means of a screw which pressed the junction firmly against the plate. The copper wires of this junction were connected through a galvanometer to a slide-wire potentiometer by which the thermoelectromotive force between the ends of the plate was compensated. The difference of potential set up by the magnetic field was determined by first measuring the electromotive force between the ends of the plate when there was no magnetic field and then measuring it again when the magnetic field was established. The difference between these two electromotive forces gave the difference of potential called forth by the magnetic field. The observations were then repeated with the magnetic field in the opposite direction. The mean of the potential differences set up by the magnetic field in the two directions was taken as the longitudinal thermomagnetic potential-difference. The magnitude of this difference of potential is not exactly the same for both directions of the magnetic field, because it is impossible to get the copper lead wires exactly on the longitudinal axis of the plate so that the transverse thermomagnetic effect cannot make a contribution to the longitudinal effect. The difference of potential from this transverse thermomagnetic effect increases the longitudinal thermomagnetic potential difference for one direction of the magnetic field and decreases it for the opposite direction of the magnetic field. The mean of the differences of potential observed with the magnetic field in opposite direction eliminates this contribution made by the transverse thermomagnetic effect. The mean of the temperatures at the two ends of the plate was taken as the temperature at which the effect was observed. This procedure is not entirely without objection for the longitudinal thermomagnetic potential-difference is not a linear function of the temperature. Since the difference of temperature between the ends of the plate amounted to only 30° or 40° C. the error introduced by this approximation is not serious. The results of the observations on bismuth are given in Table I. The same observations have been plotted in Fig. 1. It is seen from this curve that this longitudinal effect in bismuth decreases rapidly with rising temperature. The slope of the curve indicates that the effect would vanish at the melting point of bismuth. This result is not in agreeemnt with the observations of Zahn who noted an increase in the effect with rising temperature.

The potential-gradient set up by the magnetic action is in the opposite direction to the temperature-gradient in the plate. According to the usual convention this makes the effect in bismuth negative. The average value of the thermoelectromotive force of this bismuth against copper between 32° C. and 72° C. was 6.26×10^{-5} volts per degree Centigrade difference in temperature. At this temperature a magnetic field of 20,000 C.G.S. units sets up in the plate a longitudinal electromotive force which is equivalent to an increase of about 30 per cent. in the thermoelectromotive force.

Table I.

$t°$ C.	L	$t°$ C.	L
34.5°	0.116	117°	0.051
41.7	0.110	148	0.040
50.5	0.104	151	0.035
64	0.094	203	0.021
101	0.066	215	0.015

From the curve in Fig. 1 the value of L at 53° C. is found to be 0.102. This value as well as the other values in Fig. 1 is for a magnetic field of 9,600 C.G.S. units. For this same temperature and for a magnetic field of 11,000 C.G.S. units Barlow[1] found L to be 0.100,—a value in good

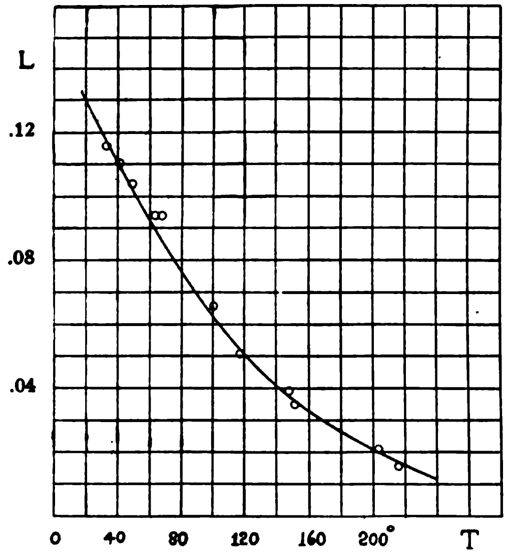

Fig. 1.

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[1] Ann. der Phys., 12, p. 897 (1903).

agreement with that noted above. For a magnetic field of 6,290 C.G.S. units Zahn found L to be 0.111 at 24.1° C. The value of L for this temperature taken from the curve in Fig. 1 is 0.128. Here the agreement is less satisfactory.

Roberts[1] has shown that when graphite is placed in a transverse magnetic field there is a very large change in its electrical resistance. Since the longitudinal thermomagnetic effect is in a way the analogue of the change in the electrical resistance in a magnetic field it seemed that this longitudinal effect in graphite might be large enough to be measured. Two plates of Acheson graphite were made. These plates were 3.2 cm. long, 1.4 cm. wide and 0.2 cm. thick. The ends were copper-plated and then soldered to copper tubes in the manner described by the author[2] in the study of the Nernst effect in alloys. A description of the apparatus accompanies Fig. 14 of the paper just cited. To the copper-plating on either end of the plate was soldered a copper-advance thermal junction so that the junctions were as nearly as possible on the longitudinal axis of the plate. The temperature-gradient in the plate was established by causing steam at atmospheric pressure to flow through one of the copper tubes and water at room temperature to flow through the other tube. The thermoelectromotive force thus established was compensated on the slide-wire potentiometer when the plate was not in the magnetic field. The potential-difference set up by the magnetic

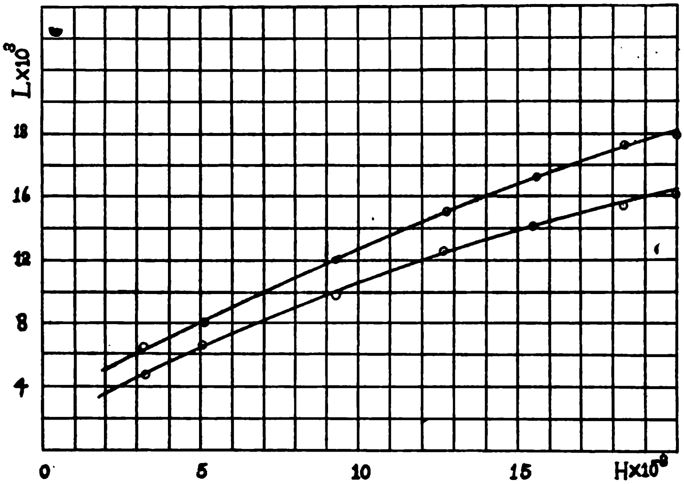

Fig. 2.

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[1] Phil. Mag. (6), 26, p. 158 (1913).

[2] PHYS. REV., 32, p. 193 (1911).

field was determined by noting the deflections of a d'Arsonval galvanometer. The magnetic field was then reversed and the deflection again noted. The mean of these deflections was taken as a measure of the potential difference set up by the magnetic action. From the figure of merit of the galvanometer the potential-difference was obtained in absolute units. The results of these observations are given in Table II. They have also been plotted in Fig. 2. One end of the plate was at a temperature of about 36° C. and the other end at about 84° C. so that the mean of these temperatures which is 60° C. may be considered the temperature at which the values of the coefficient in Table II. are given. The direction of the effect in graphite is such that the potential-gradient set up by the magnetic field is in the direction of the temperature-gradient in the plate. The effect is therefore positive in graphite. The average thermoelectric height of the graphite against copper between about 36° and 84° C. for Plate I. was 6.17×10^{-6} volts and for Plate II., 5.05×10^{-6} volts. The effect of the magnetic action was to increase somewhat the effective thermoelectromotive force in the plate. The values of L for the two plates differ from each other by about 20 per cent. The reason for this variation is probably to be found in the presence of impurities in the graphite.

TABLE II.

Plate I.		Plate II.	
H	$L \times 10^4$	H	$L \times 10^4$
3,300	65	3,250	48
5,150	80	5,100	67
9,300	121	9,300	98
12,850	151	12,700	126
15,600	173	15,600	142
18,400	193	18,300	155
20,200	197	20,200	160

Table III. contains the data on monel which is an alloy containing 68 per cent. nickel, 29.5 per cent. copper, 1.5 per cent. iron and 1 per cent. manganese. In Curve I. of Fig. 3 the potential difference in absolute units when there is a temperature-gradient of one degree Centigrade per centimeter in the plate, has been plotted against the magnetic field. In Curve II. the coefficient L has been plotted against the magnetic field. The temperature of one end of the plate was 90° C., that of the other end, 24° C. The mean temperature 57° C. may be taken as the temperature at which the values of L recorded in Table III. were determined. The thermoelectric height of monel against copper between these temperatures is 30.7 × 10^{-6} volts. In monel the effect is negative so that the potential-difference set up by the magnetic field increases the thermoelectric height of this alloy.

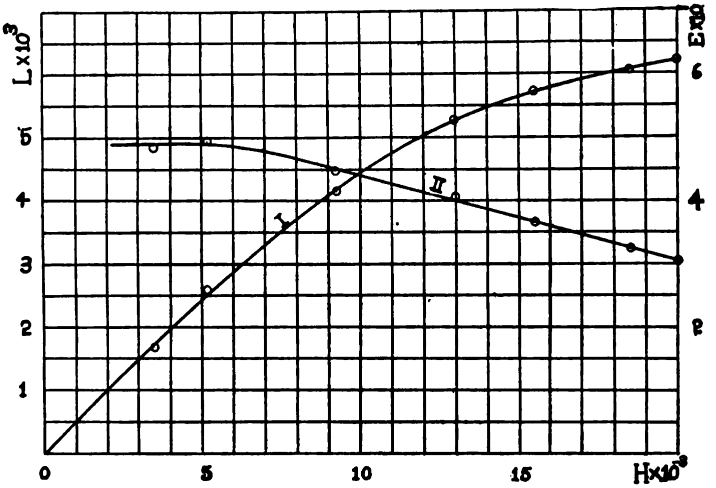

Fig. 3.

TABLE III.

H	$L \times 10^6$	H	$L \times 10^6$
3,500	484	13,000	406
5,200	498	18,500	327
9,300	448	20,000	306

The addition of antimony to bismuth causes the thermoelectric heights to pass through a maximum when the alloy contains about 9 per cent. of antimony. Curve I. of Fig. 4 shows the relation between the thermoelectric height of the alloy and the percentage by weight of antimony in it. In Curve II. of Fig. 4 the coefficient of the longitudinal thermomagnetic potential-difference has been plotted against the percentage by weight of antimony in the alloy. The value of the magnetic field in these observations was 20,200 C.G.S. units. One end of the plate was at about 72° C. and the other end at 22° C. so that the temperature at which the coefficients have been determined is about 46° C. It is seen from this curve that the coefficient of this longitudinal effect has a maximum when the alloy contains about 9 per cent. of antimony. With further addition of antimony to the alloy the coefficient decreases in a manner similar to that in which the thermoelectric heights decrease under similar condition. The two curves are, however, not parallel. The direction of the effect in these alloys is the same as its direction in bismuth.

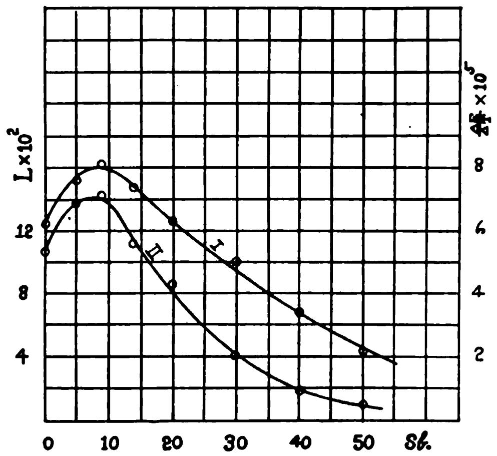

Fig. 4.

SUMMARY.

1. The longitudinal thermomagnetic effect in bismuth decreases with rising temperature and seems to vanish at the melting point of the bismuth.

2. The longitudinal thermomagnetic effect has been determined in graphite and monel. It is positive in the former and negative in the latter.

3. The longitudinal thermomagnetic potential-difference in bismuth-antimony alloys shows a maximum value when the alloy contains about 9 per cent. of antimony.

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THE MEASUREMENT OF MAGNETIC FIELDS BY THEIR DAMPING EFFECT UPON A VIBRATING COIL.

BY PAUL E. KLOPSTEG.

WHEN a coil of wire which is part of a closed electrical circuit is suspended in a magnetic field and displaced from the equilibrium position, its motion about the axis of suspension will be either periodic and damped, or if the damping is sufficiently great, the coil will approach its position of rest aperiodically. The type of motion is determined by the total resistance in the circuit. If, with a given resistance, it is periodic, the amount of damping will evidently be largely dependent upon the intensity of the magnetic field; and if the motion is to be critically damped, the intensity of the field will again be the factor which determines the resistance of the circuit for this special condition. The dependence of damping upon intensity of field is used as the basis of the work presented in this paper.

I. THEORETICAL.

1. *General.*—The various types of motion which a galvanometer moving coil suspended in the usual way may possess are represented in the general differential equation[1]

$$I_0 \frac{d^2\theta}{dt^2} + 2f \frac{d\theta}{dt} + q^2\theta = 0, \qquad (1)$$

where I_0 is the moment of inertia of the coil about its axis of suspension;
$2f$ is the coefficient[2] of damping;
q^2 is the torsional moment of the suspension fibers per unit angle of displacement;
θ is the angular displacement of the coil at the instant t.

The second term of this equation represents the total damping moment, assuming that damping is directly proportional to the angular velocity of the coil. This assumption is shown by the experimental results of this paper to be valid. A later derivation[1] shows that the first power variation law holds for that part of the damping moment which is due to the induced currents. The other part of the damping moment is due to viscosity of the air and suspension fibers and to displacement of the air in the path of the moving coil.[2]

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[1] Love, Theoretical Mechanics, 2d ed., p. 143; Jaeger, Zeitschr. f. Instrumentenk., 23, 1903, p. 262; Diesselhorst, Ann. d. Phys., 9, (4), 1902, p. 459; Ayrton and Mather, Phil. Mag., 46, (5), 1898, p. 377.

[2] "Coefficient," to distinguish this constant from the "damping factor," $\sqrt{\rho}$, used to correct the throws of a ballistic galvanometer for the damping effect.

The general solution of equation (1) is

$$\theta = \epsilon^{-at}(c_1\epsilon^{\beta t} + c_2\epsilon^{-\beta t}), \tag{2}$$

where

$$a = \frac{f}{I_0} \quad \text{and} \quad \beta = \sqrt{\frac{f^2}{I_0^2} - \frac{q^2}{I_0}}.$$

We shall consider the two cases when β is imaginary and when β is zero. The first condition is fulfilled for $I_0q^2 > f^2$, and therefore implies a value of the damping coefficient less than a certain critical value; *i. e.*, $2f < 2\sqrt{I_0q^2}$. The other condition obtains when $I_0q^2 = f^2$ or when $2f$ has the critical value $2\sqrt{I_0q^2}$. Corresponding to these two conditions are the two types of motion which are most commonly used in the ordinary moving coil galvanometer, namely, damped periodic and critically damped, or "just aperiodic."

2. *Damped Periodic Motion.*—When β is imaginary, equation (2) becomes

$$\theta = \epsilon^{-at}(A \cos bt + B \sin bt), \tag{3}$$

in which

$$b = \sqrt{\frac{q^2}{I_0} - \frac{f^2}{I_0^2}}.$$

Evaluating the constants by imposing the initial conditions which correspond to the discharge of a quantity of electricity Q through the coil at rest—this discharge imparting an initial angular velocity to the coil which is proportional to the quantity discharged, say kQ—equation (3) becomes

$$\theta = \epsilon^{-at}\left(\frac{kQ}{b} \sin bt\right), \tag{4}$$

whence the complete period

$$T = 2\pi\sqrt{\frac{I_0^2}{q^2I_0 - f^2}}. \tag{5}$$

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[1] See equation (13), p. 393.

[2] An experiment carried out in connection with this work shows that at diminished pressures, as low as 0.5 mm. of mercury, the logarithmic decrement at any given field value is practically the same as at atmospheric pressure, showing that by far the greater part of air damping is due to viscosity. The effect of viscosity is also proportional to the first power of the linear, and therefore of the angular velocity.

With no damping the complete period is

$$\tau = 2\pi\sqrt{\frac{I_0}{q^2}}. \tag{6}$$

The logarithmic decrement of the motion represented by equation (4) is usually defined as the Naperian logarithm of the ratio of any maximum displacement of the coil to the one next following. Its value is given by

$$\Lambda = \log_e \frac{\theta_n}{\theta_{n+1}} = \frac{a}{b}\pi = \frac{\pi}{\sqrt{\frac{q^2 I_0}{f^2} - 1}}. \tag{7}$$

Designating the angle $(\theta_n + \theta_{n+1})$ by Θ_1 and the angle $(\theta_{n+k} + \theta_{n+k+1})$ by Θ_{k+1}, we have also

$$\Lambda = \frac{1}{k}\log_e \frac{\Theta_1}{\Theta_{k+1}}. \tag{8}$$

By equations (5), (6), and (7)

$$T = \frac{\tau}{\sqrt{1 - \frac{f^2}{q^2 I_0}}} = \tau\sqrt{1 + \frac{\Lambda^2}{\pi^2}}.\text{[1]} \tag{9}$$

The relation between two periods T_1 and T_0 of the same coil corresponding to the two values Λ and λ of the logarithmic decrement is therefore

$$T_1 = T_0\sqrt{\frac{\pi^2 + \Lambda^2}{\pi^2 + \lambda^2}}, \tag{10}$$

which shows that in a given coil a comparatively large change is necessary in the logarithmic decrement in order that the period may be appreciably affected, both Λ^2 and λ^2 being small[2] as compared with π^2.

3. *Critically Damped Motion.*—This case, based upon the condition $I_0 q^2 = f^2$, has been discussed at length by O. M. Stewart.[3] The particular solution of equation (1) is

$$\theta = \epsilon^{-at}(c_1 + c_2 t), \tag{11}$$

which becomes

$$\theta = kQt\epsilon^{-at} \tag{12}$$

by evaluating the constants with the same initial conditions imposed as before.

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[1] Bahrdt, Physikalische Messungsmethoden, p. 112; Jaeger, Zeitschr. f. Instrumentenk., 23, 1903, p. 266.

[2] For typical values of Λ and λ see table, p. 398.

[3] Stewart, O. M., PHYS. REV., 16, (1), 1903, p. 158.

II. EQUATION FOR FIELD INTENSITY—MOTION OF COIL PERIODIC AND DAMPED.

Aside from the notation which has already been introduced, the following designations will be used:

H = magnetic field intensity;
l = mean length of coil;
d = mean breadth of coil;
n = number of turns of coil;
T_0 = complete period of coil on open circuit;
T_1 = complete period of coil on closed circuit;
R' and R = total resistance in circuit when motion of coil is periodic, expressed in C.G.S. units and ohms, respectively;
R_0' and R_0 = total resistance in circuit to produce critical damping, expressed in C.G.S. units and ohms, respectively;
M = damping moment due to current induced in vibrating coil;
Λ = logarithmic decrement on closed circuit;
λ = logarithmic decrement on open circuit.

The angle of displacement of the coil is assumed so small that its cosine remains at all times very nearly equal to unity, in order that the coil may cut the lines of force perpendicularly.[1] With this condition imposed, the rate of cutting depends upon only the angular velocity of the coil.

At any instant t when the coil has the angular velocity $d\theta/dt$, the electromotive force induced in the coil is

$$\frac{dN}{dt} = nldH\frac{d\theta}{dt},$$

and if the coil is part of a circuit of resistance R', the current will be

$$I' = \frac{nldH}{R'}\frac{d\theta}{dt}.$$

The moment of the force *due only to this induced current*, opposing the motion of the coil, is equal to $nldHI'$, or

$$M = \frac{(nldH)^2}{R'}\frac{d\theta}{dt}. \tag{13}$$

There are other factors, however, which must be included in the coefficient $2f$ of $d\theta/dt$ in equation (1).

Let m represent that part of $2f$ which is due to these other causes, *i. e.*, to eddy currents, resistance and viscosity of the air and internal friction in the suspensions; m is then the coefficient of damping when the coil swings on open circuit. Hence, on open circuit, $f = m/2$; and on closed circuit

---

[1] Using telescope and scale for reading the angle of displacement, the scale being placed at a distance of 50 cm., the deflection may become 10 cm. before the cosine of the angle differs from unity by 0.5 per cent.

$$f = \frac{(nldH)^2}{2R'} + \frac{m}{2}. \tag{14}$$

From equations (5) and (7)

$$f = \frac{2I_0\Lambda}{T_1}. \tag{15}$$

When the coil is swinging on open circuit, the coefficient of damping

$$\frac{m}{2} = \frac{2I_0\lambda}{T_0}. \tag{16}$$

By equations (14), (15), and (16), with the aid of (10), we obtain for the intensity of the magnetic field the value

$$H = K\sqrt{\frac{R}{T_0}(\Lambda - \lambda)}, \tag{17}$$

in which

$$K = \frac{2\sqrt{10^9 I_0}}{nld}.$$

III. EQUATION FOR FIELD INTENSITY—MOTION OF COIL CRITICALLY DAMPED.

The criterion for "just aperiodic" motion was given in connection with equation (12) as $2f = 2\sqrt{q^2I_0}$. As in the preceding section, the damping coefficient consists of two parts, one of which may be represented by the quantity m. Both parts of the coefficient are proportional only to the angular velocity of the coil. When the motion is critically damped, therefore, the equation of damping has the form

$$\frac{(nldH)^2}{R_0'} = 2\sqrt{q^2I_0} - m. \tag{18}$$

q^2I_0 being constant for any type of motion of the coil, its value may be obtained from equations (5) and (7):

$$q^2I_0 = \frac{4I_0^2(\pi^2 + \lambda^2)}{T_0^2}. \tag{19}$$

This together with equations (16) and (18) gives for the strength of the field:

$$H = K\sqrt{\frac{R_0}{T_0}\left(\sqrt{\pi^2+\lambda^2}-\lambda\right)}. \tag{20}$$

But λ^2 is very small as compared with π^2, hence (20) may be written in the form similar to (17):

$$H = K\sqrt{\frac{R_0}{T_0}(\pi-\lambda)}, \tag{21}$$

the constant K being the same as in (17).

IV. LIMITING VALUE OF LOGARITHMIC DECREMENT.

A comparison of equations (17) and (21), term for term, shows that when the damping has become critical, R is replaced by the limiting value R_0, and Λ by the constant π. That the constant π should represent a logarithmic decrement in an aperiodic motion seems at first sight inconsistent with the definition of logarithmic decrement as usually given; for in this case there is no second displacement beyond the null position. The following consideration will show that by adopting a somewhat different definition for the logarithmic decrement, we may consider π still to be a logarithmic decrement in the above equation.

The ordinary definition of the term as applied to the moving coil is based upon the relative magnitude of two successive displacements from the null position, taken at intervals equal to the time of a half-vibration of the coil, as shown by equation (7). Similarly,[1] we may define the logarithmic decrement of an aperiodic motion as the natural logarithm of the relative magnitude of two successive displacements taken at an interval of time equal to $\tau/2$, the half-period when there is no damping. By equation (12), at the instant T,

$$\theta_T = kQT\epsilon^{-aT};$$

and at the instant $T+\tau/2$,

$$\theta_{T+\tau/2} = kQ\left(T+\frac{\tau}{2}\right)\epsilon^{-a(T+\tau/2)}.$$

The ratio of displacements

$$\frac{\theta_T}{\theta_{T+\tau/2}} = \frac{T}{T+\frac{\tau}{2}}\epsilon^{a\cdot\tau/2} = \frac{T}{T+\frac{\tau}{2}}\epsilon^{\pi}.$$

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[1] The term "logarithmic decement" has already been applied to a non-periodic velocity (Daniell, Principles of Physics, 1911, p. 185)—a moving body, encountering a resistance which is proportional to the velocity, being negatively accelerated in such a way that during successive equal intervals of time the natural logarithm of the velocity changes by a constant amount.

As T increases, the coefficient of ϵ^{π} approaches unity, so that for values of T which are large as compared with $\tau/2$, *i. e.*, near the end of the motion, the logarithmic decrement, as defined above, becomes equal to π.

V. DISCUSSION OF EQUATIONS (17) AND (21).

It is not a difficult matter to obtain experimentally the data needed for determining a field intensity. After K has once been determined for a given coil, the measurements involve a determination of time,[1] resistance, and angular displacement. All of these enter into the formula under the radical sign, so that the probable error of the result is only half that of the observations. The constant K may be determined either by direct computation from its factors, each of which is readily obtained; or the coil may be suspended in a field of known value and the constant calculated from the observations by means of equation (17).[2] The latter method is used when the number of turns of the coil or its dimensions are not readily obtainable; incidentally, with the dimensions known, the number of turns may be calculated from this determination.

The logarithmic decrements are found by means of equation (8). The error of observation may be reduced to a minimum by taking k sufficiently large; intermediate values of the angle need not be taken, except as a means of checking the result when this is desirable. It is a well-known fact that the logarithmic decrement varies slightly with the amplitude of vibration;[3] but if the displacements are not too large, *i. e.*, approximately not greater than 10 cm. on the scale at a distance of 50 cm., the error is negligible, as shown by the experimental verification of the equations.

From theoretical considerations alone, it would seem preferable to use the periodic method of equation (17) rather than the aperiodic method of equation (21). In the first place, the aperiodic method cannot be used at all for the measurements of fields, the intensity of which is less than that for which the coil is critically damped on short circuit. Again, the observations for equation (21) are more difficult to make than those for equation (17), since it is necessary to adjust a resistance in the coil circuit to such a value that the coil returns to zero in the minimum time without passing beyond. It is difficult to judge exactly when this condition obtains. The resistance used in (17) is chosen arbitrarily, and may have any value so long as the damping is not too great to make the corresponding logarithmic decrement difficult to obtain.

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[1] The determination of the period of the coil in every measurement of field strength is necessitated by the magnetic impurities in the coil (White, PHYS. REV., 23, (1), 1906, p. 382; A. Zeleny, PHYS. REV., 23, (1), 1906, p. 399; 32, (1), 1911, p. 297; Diesselhorst, Zeitschr. f. Instrumentenk., 31, 1911, p. 247).

[2] It should be noted that when once the constant is known for any particular coil, this coil may, without redetermining K, be used with any kind of suspension; no term in the expression for K is dependent for its value upon the suspension fiber.

[3] Peirce, B. O., Proc. Am. Acad., 44, 1908, p. 72.

Experimental tests of the two equations also show the periodic method preferable to the other. Results obtained in using equation (21) have been found in a number of sets of observations to range from three to seven per cent. higher than those given by the ballistic method, the difference increasing with the field strength; as will be seen later, results of the periodic method agree to within one per cent. in almost every case. It is purposed to make a further study of equation (21) to ascertain, if possible, the reason for the observed discrepancy.

There are obviously several advantages of the damped coil method over the ballistic method, principal among which is the simplicity of the apparatus necessary for the determinations. Another is its adaptability to the measurement of a galvanometer field containing an iron core,[1] since the coil will swing as readily about the core as in a free space; furthermore, in a galvanometer field the assumption originally made, namely, that at any instant the coil cuts the lines of force perpendicularly, is more nearly fulfilled than in parallel fields.

VI. Experimental.

To test the accuracy of the method given above, the values obtained by its use for a series of magnetic fields were compared with determinations of the same fields by the ballistic method.

For the purpose of obtaining a variable field of known intensity, an electromagnet with large plane pole pieces was used. The field intensity corresponding to any given current in the electromagnet was first measured by the ballistic method with a test coil of about 10 sq. cm. area having 30 turns. The coil was placed between the poles of the electromagnet, and by means of a rubber band quickly rotated through a half revolution when a release was operated. Throws from the test coil were compared with throws from a standard mutual inductance coil,[2] the coefficient of which had been accurately determined. The primary current in the comparison coil was measured by means of a standard resistance and potentiometer. In order to obtain a definite strength of field with any given current the magnet was, at the beginning of any determination, subjected to several cycles of hysteresis, after which the current was increased. The demagnetizing current necessary to overcome the coercive force of the iron was accurately determined, so that zero field could be obtained at will. The magnetization curve was carefully drawn to a large scale, and from it were taken the field values with which the results of the damped coil method were compared.

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[1] A similar method of obtaining H in galvanometer fields has been suggested by White (Phys. Rev., 23, 1906, pp. 390–392), who gives an equation for such a determination. Some of the quantities entering into the equation are, however, difficult to obtain or to estimate with certainty. According to White, the error arising from the use of his formula "seldom exceeds ten per cent."

[2] Zeleny, A., Phys. Rev., 23, 1906, p. 411.

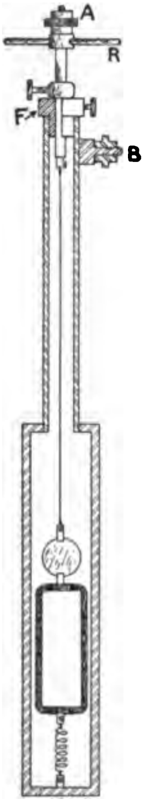

Fig. 1.

For the measurements of field intensities by the damped coil method the arrangement shown in the figure was used. This consists simply of a brass box for supporting a d'Arsonval galvanometer coil (Leeds and Northrup, type H or P) with its upper and lower suspensions. The lower part is square with one side covered with glass, the upper part is tubular. The top post is insulated by the plug *F*, and *A* and *B* are the binding post connectors. The box was supported by a non-magnetic clamp in the space where the magnetic field was to be measured. The galvanometer coil (395 turns, 4.85 × 1.69 cm.) with its suspension had a resistance of 121.7 ohms. The desired displacements of the coil were obtained by sending through it one or more discharges of a ½ mf. condenser charged by a cell. The coil could, by means of a double-throw switch, be thrown at will into the condenser or resistance circuit. It is essential to have the suspensions free from torsion when the coil is in the null position, which is accomplished by first suspending it from the upper suspension alone.

The readings for logarithmic decrements were obtained by means of a telescope and circular scale of 50 cm. radius, placed at a distance of 50 cm. from the mirror. Periods were measured by means of a rated stopwatch. The moment of inertia of the coil was found by comparing its period with that of an accurately turned brass disk of approximately the same mass, each in turn suspended by means of the same 1.5-mil phosphor bronze fiber. I_0 was found to be 3.20 C.G.S. units, and the factor *K*, 34.80.

A comparison of the results obtained for a series of fields by the two methods is given in the last two columns of the accompanying table. The other columns give data in connection with the damped coil method. The values given for *H*, as obtained by this method, are in each case the average of three determinations with different resistances in the circuit. Only one of these resistances and the corresponding value of Λ is given for each field. The three determinations for every field were in agreement to a fraction of one per cent.

Magnetizing Current.	T_0	λ	R	Λ	H (Damped Coil Method).	H (Ballistic Method).
0.0998	7.948	.01102	121.7	.01170	3.404	4.4 (about)
0.1199	7.945	.01101	121.7	.02242	14.54	16.5 (about)
0.1885	7.967	.01128	121.7	.18720	57.0	57.0
0.263	7.974	.01190	621.7	.1277	104.5	105.7
0.332	7.948	.01278	1,122	.1399	147.4	148.5
0.414	7.890	.01413	1,622	.1747	199.8	199.0
0.566	7.478	.01742	3,500	.1708	294.7	295
0.983	6.913	.03060	10,000	.2026	548.5	542
1.421	6.428	.04614	20,000	.2079	780	770
1.854	6.128	.06196	40,000	.1800	966	964
2.350	5.891	.07769	50,000	.2025	1,133	1,143
3.500	5.630	.09800	100,000	.1892	1,400	1,405
4.330	5.503	.10678	100,000	.2129	1,528	1,503

Not considering the first two weakest fields given in the table for which the ballistic method gave only approximate values, it is seen that the results of the two methods are in as good agreement as the accuracy of the ballistic method allows.

VII. Summary.

Briefly, the foregoing paper is a presentation of the following:

1. Derivation of an equation for the intensity of a magnetic field in terms of quantities readily obtainable by observations upon a suspended coil vibrating in the field with damped periodic motion.

2. Derivation of a similar equation, depending upon critical damping; and an application of the term "logarithmic decrement" to critically damped motion of a moving coil.

3. Experimental verification of the equations, showing that the method depending upon damped periodic motion may be applied with an accuracy of at least 1 per cent. to the measurement of fields ranging from a few lines to at least 1,500 lines per cm., using the same coil over the entire range.

Physical Laboratory,
The University of Minnesota,
October 1, 1913.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SIXTY-EIGHTH MEETING.

A REGULAR meeting of the Physical Society was held in Fayerweather Hall, Columbia University, New York, on Saturday, October 18, 1913.

Vice-president Merritt presided at the meeting.

At the morning session the following papers were presented:

The Vapor Pressure of Metallic Tungsten. **Irving Langmuir.**

The Form of the Ionization by Impact Function $a/p = f(x/p)$. **Bergen Davis.**

Change of State Solid-Liquid at High Pressure. **P. W. Bridgman.**

Notes on Some Integrating Methods in Alternating Current Testing. **Frederick Bedell.**

Silvered Quartz Fibers of Low Resistance Obtained by Cathode Spray. **Horatio B. Williams.**

The Critical Ranges $A2$ and $A3$ of Pure Iron. **G. K. Burgess** and **J. J. Crowe.**

A Spectrophotometric Study of the Absorption, Fluorescence and Surface Color of Magnesium-Platinum Cyanide. **Frances G. Wick.**

Examination of the Omnicolore Screen Plate by Means of Microscope and Spectroscope. **John B. Taylor.**

Relativity Theory; General Dynamical Principles. (By title.) **Richard C. Tolman.**

The Hall Effect in Liquid and Solid Mercury. **W. N. Fenninger.**

Failure of Color Photography by Commercial Screen-Plate Methods for Spectroscopic Records. **John B. Taylor.**

Some Experiments on the Magnetic Field of Two Electromagnets in Rotation. **S. J. Barnett.**

(Adjourned at 1:00 P. M. for lunch.)—Afternoon Session.

An Electrolytic Determination of the Ratio of Silver to Iodine and the Value of the Faraday. **G. W. Vinal** and **S. J. Bates.**

Effect of Amalgamation on the Contact E.M.F. of Metals. **F. J. Rogers.**

Relativity Theory; The Equipartition Law in a System of Particles. (By title.) **Richard C. Tolman.**

Condition Involving a Decrease of Primary Current with Increasing Secondary Current. F. J. Rogers.

The Effect of Space Charge and Residual Gases on the Thermionic Current in a High Vacuum. Irving Langmuir.

It was voted to approve the recommendation of the Council that in the case of the annual meeting, the Washington meeting and the Chicago meeting a local committee be given charge of the program for one half-day session, the appointment of this committee to be made by the president of the Society.

Adjourned at 4:30.

Alfred D. Cole,
Secretary.

CHANGE OF STATE SOLID-LIQUID AT HIGH PRESSURES.[1]

By P. W. Bridgman.

The melting temperature and the difference of volume between liquid and solid has been measured as a function of pressure for the following eleven substances: potassium, sodium, carbon dioxide, chloroform, anilin, nitrobenzol, diphenylamine, benzol, carbon tetra-chloride, orthokresol, and phosphorus. The range of the experiments is from 0° to 200°, and up to 12,000 kgm/cm^2. The melting curves (melting temperature against pressure) all are concave toward the pressure axis, the curvature becoming less at the higher pressures. The change of volume curves are also all similar to each other, but are different from the melting curves in that they are all convex toward the pressure axis. These two facts, together with Clapeyron's equation, indicate that at still higher pressures we are to expect neither a maximum nor a critical point, but that in all probability the melting curve continues to rise indefinitely.

In addition to the experiments on the transition liquid-solid, new allotropic modifications of the solid were found for four of the substances. Benzol and orthokresol have one new form stable at high pressures, carbon tetrachloride has two new forms, and there are two new forms of phosphorus, one of which changes reversibly into the ordinary yellow phosphorus under the proper conditions, but the other is obtained from the yellow variety by an irreversible reaction at high pressures and temperatures, and is stable under atmospheric conditions. This new form is in appearance like graphite, and has the density 2.60.

The Jefferson Physical Laboratory,
Cambridge, Mass.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

SILVERED QUARTZ FIBERS OF LOW RESISTANCE OBTAINED BY CATHODE SPRAY.[1]

BY HORATIO B. WILLIAMS.

LOW resistance quartz fibers suitable for use in the Einthoven galvanometer and similar instruments, are usually prepared by chemical silvering. Such deposits are rough and the amount of silver is high in proportion to the conductivity. Cannegieter has shown that smooth fibers can be produced by deposition of a cathode film, followed by electroplating. By the method here outlined, fibers of low resistance can be obtained by the cathode spray alone, thus diminishing the number of manipulations and avoiding all contact with chemical solutions. The cathode is of pure sheet silver bent to a half cylinder. The fibers are held in the discharge tube on a glass frame to which they are cemented with hot shellac. The tube is several times exhausted to .01 mm. and rinsed with dry electrolytic hydrogen. Discharge is maintained at .01 ampere with voltage from 1,200 to 1,500. Direct current is supplied by two small generators with armatures connected in series and fields separately excited. Much gas seems to be occluded during the discharge and a small stream of hydrogen is allowed to leak in steadily, maintaining the current constant. The time of discharge varies with the thickness of film desired. A fiber 140 mm. long, .002 mm. finished diameter with a resistance of 2,700 ohms was obtained by exposure for three hours. The fibers are microscopically smooth and the coating is very compact, uniform and strongly adherent. A liquid air block between the discharge tube and the other parts of the apparatus insures uniform success, but good results can sometimes be secured without it.

DEPARTMENT OF PHYSIOLOGY,
COLUMBIA UNIVERSITY, NEW YORK.

THE EFFECT OF SPACE CHARGE AND RESIDUAL GASES ON THE THERMIONIC CURRENT IN HIGH VACUUM.[1]

BY IRVING LANGMUIR.

THE mutual repulsion of electrons (space charge) in a space devoid of positive ions limits the current that flows from a hot cathode to a cold anode. For parallel plane electrodes of infinite extent, separated by the distance x, and with a potential difference v between them, the maximum current (per unit area) that can flow if no positive ions are present is

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\,\frac{v^{\frac{3}{2}}}{x^2}.$$

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

For the analogous case of an infinitely long hot wire placed concentrically within a cylindrical anode of radius r, the maximum current per unit length is

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{v^{\frac{3}{2}}}{r\beta^2},$$

when β varies from 0 to 1, according to the diameter of the wire, but for all wires less than one tenth of the diameter of the anode, β is extremely close to unity.

Experiments show that in a very high vacuum (pressure less than .0001 mm.) and with electrodes which do not give off gas the space charge limitation often prevents the thermionic currents from exceeding a few milliamperes. Pressures of gas as high as .001 mm. with voltages above 40 volts usually lead to the formation of sufficient positive ions to neutralize the effect of space charge.

The presence of low pressures of most gases (.001 mm. or less) greatly decreases the electron emission from tungsten. This effect is especially marked at lower temperatures and tends to disappear at very high temperatures. This results in an increase in the value of b of Richardson's equation produced by practically all gases except the group of inert gases.

The proper conditions for obtaining the normal thermionic current from heated metals are discussed. This electron emission is found to be a true property of the pure metal and is not due to secondary chemical effects. For tungsten the thermionic current varies with the temperature in full accordance with Richardson's equation with the following constants:

$$a = 34 \times 10^6 \text{ amps. per sq. cm.,}$$

$$b = 55{,}500.$$

Pure electron currents, of even several tenths of an ampere without any perceptible positive ionization, are thus readily obtained. No disintegration of the cathode occurs under these conditions.

The effect of nitrogen in decreasing the thermionic current depends on the voltage of the anode. In many cases much less current is obtained at high than at lower voltages.

The following theory is in full accord with the observed phenomena: The effect of gases in changing the saturation current is due to the formation of a film of an unstable compound on the surface of the metal. The extent to which the surface is covered depends on the relative rates of formation and of destruction of the film. The film may be formed by direct reaction of the metal with the gas or be produced by the bombardment of the metal by positive ions. The film is destroyed by decomposition, volatilization, or cathodic sputtering (bombardment by positive ions).

Research Laboratory,
General Electric Co.,
Schenectady, N. Y.

NOTES ON SOME INTEGRATING METHODS IN ALTERNATING CURRENT TESTING.[1]

BY FREDERICK BEDELL.

AN alternating current or voltage can be measured by a direct current instrument or galvanometer of the D'Arsonval type if a synchronous commutator is interposed between the circuit and the instrument. The reading of the instrument is the integral of the alternating current for half a period, the limits of the integral being determined by the setting of the brushes on the commutator. The brushes may be shifted so as to shift the half period over which the integral is taken. In this way successive instantaneous values may be found of one quantity the value of which depends upon the integral of the quantity directly measured. For example, if the quantity measured by means of the commutator and galvanometer is the current flowing in a condenser, the successive readings of the galvanometer are proportional to the instantaneous values of the charge q of the condenser, since $q = \int i dt$. The integral readings of condenser current for any setting of the brushes gives the instantaneous value of q at the moment of commutation. Since potential v is proportional to q, this gives a method for determining the wave-form of potential. If the potential is taken across the terminals of a non-inductive resistance, the wave-form of current is determined.

This condenser current method for determining wave-form is much more sensitive and has a much wider range than various time-honored point-by-point methods. In this and in other integrating methods[2] variation in commutator resistance may be a source of error which may be reduced by perfecting the apparatus or may be made ineffective by choice of method.

CORNELL UNIVERSITY,
ITHACA, N. Y.

THE CRITICAL RANGES *A2* AND *A3* OF PURE IRON.[1]

BY G. K. BURGESS AND J. J. CROWE.

IN spite of a great amount of experimental work and even more theorizing, the question of the allotropy of iron is not yet satisfactorily settled. The separate existence of the lower critical range *A2* has been seriously questioned by several recent writers; nevertheless all the physical properties of iron which have been studied, with the single notable exception of crystallo-

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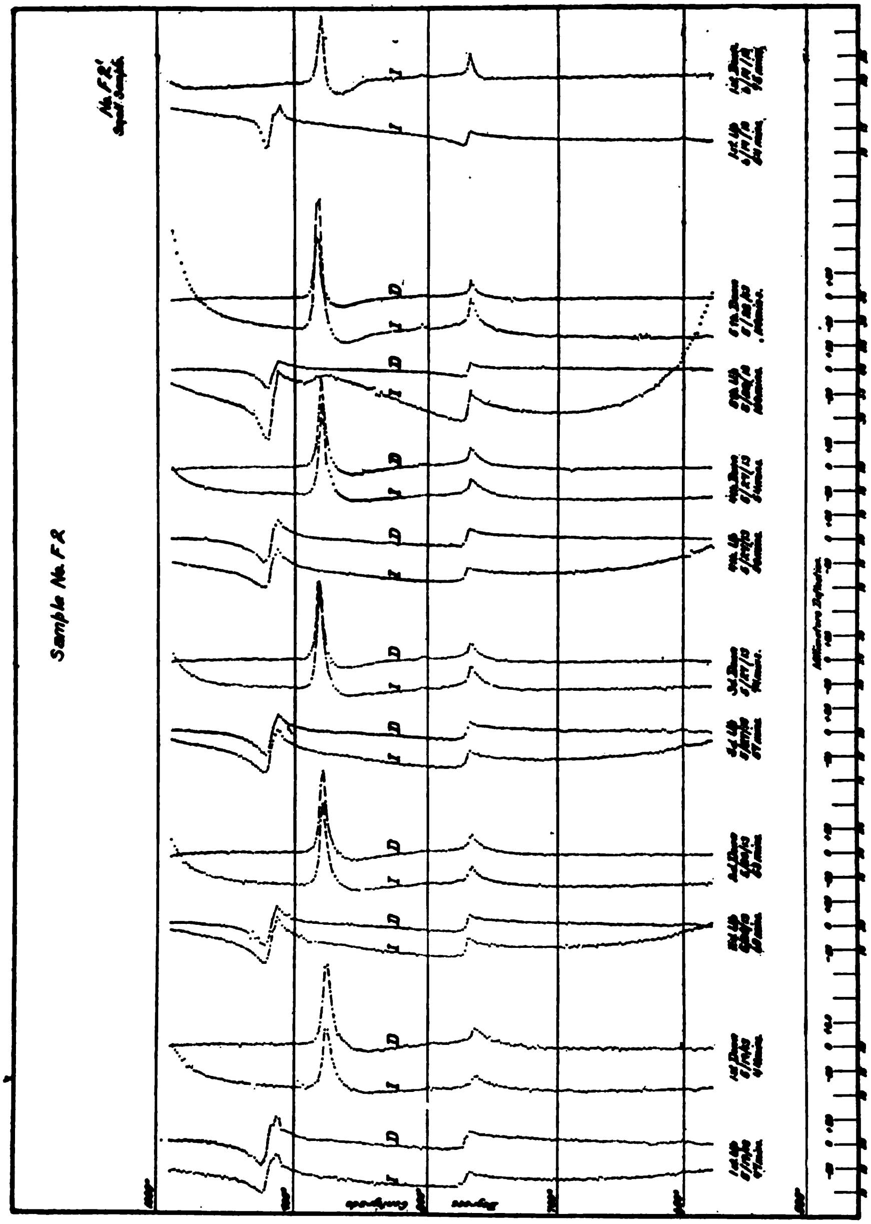
[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

[2] For a detailed description of these methods, see the following papers by F. Bedell: "Condenser Current Method for the Determination of Alternating Wave Form," The Electrical World, August 23, 1913; "The Use of the Synchronous Commutator in Alternating Current Measurements," Journal of the Franklin Institute, October, 1913


Sample No. F2
No. F2'
Small Sample
Amplitude
Degrees
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I
Millimetre Deflection
Time in Seconds

graphic structure, have shown, in the hands of one or more skillful experimenters, a distinct discontinuity for the lower critical range *A*2 as well as for the upper *A*3 range. For several of the phenomena, such as electrical resistance, thermo-electricity, specific heat, and magnetism, it would appear that the discontinuity is at least as great for *A*2 as for *A*3, while the thermal effect has of course been long recognized as being much the more pronounced at *A*3.

This investigation consisted in taking in vacuo some 130 heating and cooling curves by two methods simultaneously, the inverse rate and differential for 15 samples of pure iron prepared by various methods and analyzed by several chemists. Unusual precautions were taken to secure uniformity of heating of the samples, and it was also possible to take observations for samples of widely different mass and over a wide range of rates each maintained strictly constant. Two furnaces were used and temperatures were taken with six separately calibrated thermocouples. The observations show that in order to get consistent and reliable results in the thermal analysis of a substance such as iron, the properties of which are so readily susceptible to many minor influences, it is necessary to get rid of all the disturbing influences.

We find essential the following precautions:

1. The iron should be pure; our purest samples were 99.983 and contained 0.003 per cent. carbon or less; and it should be kept pure by heating it only in vacuo; a pressure of 0.01 mm. Hg suffices.

2. Either the occluded gases should be removed by premelting the iron, preferably in vacuo, or it will in general be found necessary to take a series of heating and cooling curves at widely different rates, in order to determine correctly the location of the critical ranges *A*3 and *A*2.

3. The iron should be in a single piece entirely surrounding and in contact with the thermocouple junction, otherwise the thermocouple will integrate the irregular progress of the heat through the sample and the curves will lose their sharpness; small samples (1.0 gram or so) give sharper results than large samples.

4. The interval of recording temperatures should be wide enough that sufficient sensibility is attained and narrow enough that the contour of the curves is not distorted; we have found a 2° interval satisfactory.

5. The sensibility of the apparatus indicating temperature and differences of temperature should be of the order of 0.01 degree and time should be measured to better than 0.2 second.

Among the results of this investigation may be mentioned the demonstration that the inverse rate and differential methods, the latter plotted as the derived differential curve, give identical results of the same sensibility for the critical ranges, and the two sets of curves are strictly similar, save for minor particulars.

The plotted curves give what seems to us conclusive evidence of the independent existence of *A*3 and *A*2, all of the 130 curves without exception showing both these critical ranges sharply defined and unquestionably distinct.

It was found impossible to eliminate or attenuate *A*2 by thermal treatment. The *A*2 transformation has not a double cusp, nor do there appear to be other transformations above *A*3 and below *A*2 between 300° and 1050°. With electrolytic iron, unless the sample has been premelted into a compact mass, erratic results will be obtained for both *A*3 and *A*2, the location of the critical points apparently depending in the main upon the rate of heating or cooling. The critical points may even be displaced by over 50°. It is possible, however, to reduce the observations on untreated electrolytic iron to exactly the same temperature basis as the gas-free, compact material by taking curves at several rates and reducing to zero rate. This would appear to indicate that the gases occluded, mainly hydrogen, play no essential chemical rôle in modifying the iron equilibrium.

Even with gas-free iron the *A*3 point is not entirely independent of the rate of heating or cooling, so that it is necessary to reduce the observations to zero rate in order to obtain correct results for *Ac*3 and *Ar*3. The range in the location of *Ar*3, for example, with premelted samples was found to be 876° C. at 0.155 deg./secs. to 897° C. at zero rate.

All preparations of pure iron, even those containing gases, when reduced to the common basis of zero rate of heating or cooling, have the same maximum for the *A*2 critical range, namely, $A2 = Ac2 = Ar2 = 768° \pm 0.5$. All but one of the 15 samples gave this result to within 2°, the other to 3°.

Similarly for zero rate, the value of the maxima of *A*3 are found to be $Ac3 = 909° \pm 1$ and $Ar3 = 898° \pm 2$.

It was not possible to infer a single equilibrium temperature *Ae*3 from these experiments, the *Ac*3 transformation on heating always being at a higher temperature than *Ar*3, the transformation on cooling.

It was found, however, that the beginning of *Ac*3 coincides in temperature with the beginning of *Ar*3 as closely as could be judged. It is as if the crystallographic change at *A*3 required, so to speak, a temperature inertia to complete itself both on heating and on cooling, although the effect of rate on the equilibrium appears to be slightly the greater on cooling.

It is possible that the *A*3 transformation is somewhat more complex than this as there are indications from some of the heating curves of a doubling of *Ac*3 although not of *Ar*3. This effect may be fortuitous.

The relative amounts of heat accompanying the two transformations, *A*3 and *A*2, is approximately ^{2} to ^{1} respectively.

An examination of some of the heating curves will perhaps give the erroneous impression that *Ac*2 is an evolution rather than an absorption of heat. The swing back at the maximum is very abrupt following what appears to be a gradual building up of this maximum from an indeterminate low temperature. This behavior would be in accordance with the gradual change in certain physical properties, such as magnetism and electrical resistance, as *A*2 is approached. On the other hand, the operations carried out on sample *F*2 failed to diminish sensibly the intensity of *Ac*2, which would imply that this thermal transformation is limited to a narrow temperature interval; also some of the curves of $Ac3$ show that this long back swing appears to be in part at least a property of the heating conditions. The shading off on cooling through $Ar2$, if this effect is a real one, might be marked by a similar swing back from this peak, and therefore be indistinguishable.

We hesitate to express an opinion on the nature of the allotropy of iron. The fact that $A2$ appears to be accompanied by no crystallographic change, such as accompanies $A3$ requiring a violent rearranging of relatively large crystal masses and involving a considerable quantity of heat, may account for the sharpness with which $Ac2$ equals $Ar2$, and the $A2$ transformation may be merely molecular not involving the crystallographic structure as such. Whether we have any β iron or not to inhabit the region between $A2$ and $A3$ will depend on our definition of allotropy, but we hope that we have proved beyond a reasonable doubt that under standard conditions there is a definite transformation at 768° and a less well defined although more intense one at 898° to 909° in terms of their maxima on cooling and heating, respectively.

BUREAU OF STANDARDS,
WASHINGTON,
September 2[illegible], 1913.

Second Series *December, 1913* *Vol. II, No. 6*

THE

PHYSICAL REVIEW.

A POWERFUL RÖNTGEN RAY TUBE WITH A PURE ELECTRON DISCHARGE.

By W. D. Coolidge.

§ 1. Introduction.

IN an earlier publication attention has been called[1] to the use of wrought tungsten for the anticathode, or target, of a Röntgen tube of the ordinary type. In the development of this target many different designs were made and mounted in tubes, and these tubes were operated on what was then the most powerful Röntgen apparatus on the market, a 10 K.W. transformer coupled to a mechanical rectifying device. The operation of tubes in this manner, to see how much energy it took to ruin the target, gave perhaps an unusual viewpoint. When, as a result of these experiments, a satisfactory form of target had been developed, the writer became interested in studying the remaining limitations in the tube. Some of these limitations are the following:

1. With low discharge currents the vacuum gradually improves, with a consequent increase in the penetrating power of the rays produced.

2. With high discharge currents there are very rapid vacuum changes, sometimes in one direction and sometimes in the other.

3. If a heavy discharge current is continued for more than a few seconds the target is heated to redness and then gives off so much gas that the tube may have to be reëxhausted.

4. If the temperature of the standard copper-backed target is allowed to get up to bright redness, a rapid deposition of metallic copper begins to take place on the bulb, continuing for some time after the cutting off of the current, owing to the very slow rate of cooling from such temperatures in the evacuated space.

5. Of the tubes tested, very many have failed from cracking of the

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[1] Coolidge, Trans. Am. Inst. E. E., June, 1912, pp. 870–872.

glass, and this, with one exception, always at the same point; that is, in the zone around the cathode. In many cases there has first been chipping-out of the glass from the inner surface of the tube at this point.

6. The focal spot on the target in many tubes wanders about very rapidly.[1] In many cases where it does not show a tendency to wander, it will be found after a heavy discharge to have permanently changed its location.

7. While it is relatively easy to lower the tube resistance by means of the various gas regulators, it is a relatively slow matter to raise it much.

8. With very heavy discharges, the central portion of the usual massive aluminum cathode melts, and the molten globules so formed are shot right across the tube, flattening themselves out on the glass and sticking to it. When the melted area is small, no harm is done except that the curvature of the cathode at this point may be changed, and the focal spot may, in consequence, be moved.

9. No two tubes are exactly alike in their electrical characteristics.

10. The characteristics are in general far from ideal, in that the penetrating power of the Röntgen rays produced, changes with the magnitude of the discharge current.

11. When operated on a periodically intermittent current, even though it be of constant potential, the tube, of necessity, gives a very heterogeneous bundle of primary Röntgen rays, for the reason that the breakdown voltage of the tube is much higher than the running voltage.[2]

It was found that limitations 3 and 4 could be removed by the use of a massive all-tungsten (in place of the usual copper-backed) target. Such a target can be run continuously at intense white heat. Aside from eliminating the troubles incident to the use of copper, the all-tungsten target does not change the general characteristics of the tube.

An attempt was made to remove limitation 8, imposed by the low melting point of aluminum, by substituting for it a tungsten cathode of the same dimensions. Tubes made up in this way showed a behavior entirely different from that of the ordinary tube. They would have been absolutely hopeless from the standpoint of a practical radiographer. They were like the ordinary Röntgen tube which is in the condition which the radiographer describes as "cranky." Upon passing a discharge current of any magnitude through the tube, the resistance would quickly rise to a point where, even with an impressed potential difference of 100,000 volts, no further discharge would pass. The tube could be restored to its original condition by the liberation of gas from the vacuum regulator. The phenomena would repeat themselves as often as one cared to make the experiment. Continuous operation for even a few seconds seemed out of the question. It finally developed, however, that with the adoption of the following expedient, the situation changed. Gas was admitted from the regulator and a discharge passed through the tube. As soon as the resistance had risen, more gas was admitted and the tube was again excited. These operations were repeated as rapidly as possible. With each excitation of the tube, the cathode became hotter. There was evidently the same focusing of the positive ions bombarding the cathode as there was of the electrons at the anticathode, for there was a similar localization of heat at the two electrodes. A little conical depression which formed at the center of the cathode showed that, with the vacuum range employed, the positive ion bombardment was, at least mainly, confined to an area only about 2 mm. in diameter. As soon as the cathode had become heated to bright incandescence,[1] the behavior of the tube changed, and it could then be operated continuously for at least several minutes. Upon interrupting the discharge for a short time, and so allowing the cathode to cool, the "cranky" condition returned, and the tube could again be operated continuously only after repeating the procedure outlined above.

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[1] In radiographic work, movement of the focal spot during an exposure is of course detrimental to good definition.

[2] See F. Dessauer, Phys. Zeitschr., *14*, pp. 246–247 (1913).

Tubes like the above with tungsten cathodes showed, upon operation, a rapid blackening of the bulb. The deposit proved to be metallic tungsten. The conical depression which invariably formed at the center of the cathode seemed to indicate that this was the source of the deposit, the disintegration of the metal at this point being doubtless due to the mechanical action of the positive ions which bombard it.

The extreme instability of vacuum attendant upon the use of a tungsten cathode in what was otherwise a standard Röntgen tube, called attention very forcibly to the part which is played by gases in the ordinary aluminum cathode. (The tungsten cathodes used must have been, from their method of manufacture, relatively very free from gas.)

A consideration of the above-mentioned limitations showed that they were for the most part incident to the use of gas and that they could therefore be made to disappear if a tube could be operated with a very much higher vacuum. In this case the electrons would have to be supplied in some other way than by bombardment of the cathode by positive ions.

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[1] The magnitude of the heating effect at the cathode was much greater with tungsten than it is with aluminum cathodes. In one case the cathode and the anode, which functioned also as anticathode, were both made of tungsten, exactly alike in size and shape and symmetrically placed in the tube (concave faces towards each other). On continuous operation, both ran at white heat, and, as nearly as the eye could judge, at the same temperature. Where aluminum is used as the cathode material, much less heat is developed in the cathode than in the target. Willey (Vernon J. Willey, Archives of the Roentgen Ray, XII., p. 250, 1908) finds in tubes of the ordinary type that 75 to 85 per cent. of the total heat evolution in the tube, inclusive of the glass walls, takes place at the target.

Richardson[1] and others had shown that electrons might be produced by simply heating the cathode. But the values of the thermionic currents obtained by different observers had varied between wide limits, so much so as to suggest that a Röntgen tube based upon this principle might be as unstable in resistance as is the standard tube. Moreover, the fact that the substances usually worked with, platinum and carbon, are so difficult to completely free from gas, suggested strongly that with the cleaner conditions (greater freedom from gas) that could be realized by the use of tungsten, the thermionic currents might cease altogether.[2] Some experiments of Dr. Irving Langmuir,[3] however, on the thermionic currents between two tungsten filaments in a highly evacuated space, were very reassuring. According to his observations, after a certain high degree of exhaustion had been reached, the thermionic currents increased, up to a certain limiting value, as the tube became freer and freer from gas.

The idea of using a hot cathode in a Röntgen tube was not new, but, so far as the writer could learn, the principle had never been successfully applied in a vacuum good enough so that positive ions did not play an essential rôle.

Wehnelt and Trenkle[4] had used a hot lime cathode for the production of very soft Röntgen rays, working with voltages from 400 to 1,000. Wehnelt, in another article, describes the use of his lime cathode in a Braun tube, and here he says that it is not advisible to employ more than 1,000 volts, as otherwise cathode rays come off from that part of the platinum which is bare, giving bad disintegration.

The Röntgen rays produced by voltages as low as 1,000 are of course too "soft" for the ordinary applications.

Lilienfeld and Rosenthal[5] had described a Röntgen tube whose penetrating power is, they say, independent of vacuum. Their main aluminum cathode and their platinum anticathode are shaped and located like the electrodes in the ordinary Röntgen tube. Besides these they have an anode and an auxiliary hot cathode. Current from a low voltage source passes from the hot cathode to the anode and this current furnishes the positive ions which by their bombardment of the main cathode liberate electrons from it. Their tube is dependent for its operation on the presence of positive ions, for without these there is no means provided for getting electrons out from the main, aluminum, cathode. Lilienfeld concludes from his extended experiments in tube exhaustion that the complete removal of all gas from tube and electrodes would not do away with positive ions. There would according to this view be no such thing as a pure electron discharge. Lilienfeld's work in exhausting the gas from the tube itself and from the glass seems to have been excellent, but according to the experience of the writer, his electrodes were not sufficiently freed from gas to justify the conclusions drawn. Working even with tungsten electrodes in a tube so designed that the electrodes could be heated in place to very high temperatures, the writer has had the positive ion effects persist for hours, disappearing completely however as the electrodes become sufficiently freed from gas.

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[1] Proc. Camb. Phil. Soc., XI., 286 (1902); Proc. Roy. Soc., LXXI, pp. 415–418 (1903).

[2] See Goldstein, Ann. der Physik, *24*, p. 91, 1885. He finds that platinum must be heated almost to its melting point to give an appreciable thermionic current. Also see H. A. Wilson, Proc. Roy. Soc., *72*, pp. 272–276 (1903). He concludes with the following statement: "It is probable that a pure platinum wire heated in a perfect vacuum would not discharge any electricity at all, either positive or negative, to an extent appreciable on a galvanometer."

[3] This work is just being published.

[4] A. Wehnelt and W. Trenkle, Sitzungsber. d. Phys.-Medic. Soc. in Erlangen, *37*, 312–315 (1905).

[5] J. E. Lilienfeld and W. J. Rosenthal, Fortschritte auf dem Gebiete der Röntgenstrahlen, *18*, 256–263 (1912).

The work of Dr. Langmuir had shown that a hot tungsten cathode in a very high vacuum could be made to continuously yield a supply of electrons at a rate determined by the temperature.

Further work showed that very high voltages, up to at least 100,000, in no wise affect this rate of emission. For application to the fields of radiography and fluoroscopy, it was necessary to develop a satisfactory method of focusing. And, finally, the large amounts of energy transformed into heat in a Röntgen tube render imperative the use of a very heavy target, and this made it necessary to develop methods for sufficiently freeing from gas large masses of metal.

The result of efforts in this direction has been entirely successful, and tubes have been made, based upon this principle, which are free from all of the above-mentioned limitations. This is of particular physical interest because it brings all of the peculiarities of the Röntgen ray tube into accord with the modern conception of electronic conduction and gas molecule decomposition In the following, it will be sufficient to describe one type (a focusing tube) and its characteristics, leaving for later papers the description of other types.

§ 2. GENERAL DESCRIPTION OF THE NEW TYPE OF TUBE.

The structural features of the new tube which differ from those of the ordinary type are the following:

The pressure, instead of being, as in the ordinary tube, a few microns, is as low as it has been possible to make it, that is, not more than a few hundredths of a micron.

The cathode consists of a body which can be electrically heated (such as a tungsten or tantalum filament) and, suitably located with reference to this portion, an electrically conducting ring or cylinder, consisting preferably of molybdenum or tungsten or other refractory metal. The ring or cylinder is connected either to the heated portion of the cathode, or to an external source of current by means of which its potential may be brought to any desired value with respect to the heated portion. The heated portion of the cathode serves as the source of electrons, while the ring or cylinder assists in so shaping the electrical field in the neghborhood of the cathode that the desired degree of focusing of the cathode-ray stream upon the target shall result.

The anticathode, or target, functions at the same time as anode.

The operation is satisfactory only when the vacuum is exceedingly high, so high that the ordinary tube would carry no current even on 100,000 volts.

§ 3. Theory of Operation.

As will be seen from the characteristics of the tube, in § 5, it gives, in operation, no evidence of positive ions. This makes the theory of its operation exceedingly simple.

The discharge appears to be purely thermionic in character.

The rate of emission of electrons from the filament appears to be in accord with Richardson's Law, which says that the maximum thermionic current, which can be drawn from a hot filament is

$$i = a\sqrt{T}e^{-\frac{b}{T}}$$

where T is the absolute temperature, e is the base of the natural system of logarithms, and a and b are constants.

In the particular tube described in detail in this paper, over the range of temperatures and voltages included in the data of Table I., this simple law accounts perfectly for the conductivity of the tube. With still higher temperatures, however, the discharge currents would be found to increase at a much slower rate than that required by the above law. And the same applies, even in the temperature range of Table I., to a different tube design in which the distance between cathode and anode is greater. In these cases the failure to follow Richardson's Law at the higher temperatures has been accounted for by Dr. Langmuir[1] by the spacial density of negative electricity in the neighborhood of the cathode.

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[1] L. c.

§ 4. Detailed Description of Tube No. 147.

This description relates to tube No. 147, which was used in getting the data for the following tables. Fig. 1 shows a complete assembly, while

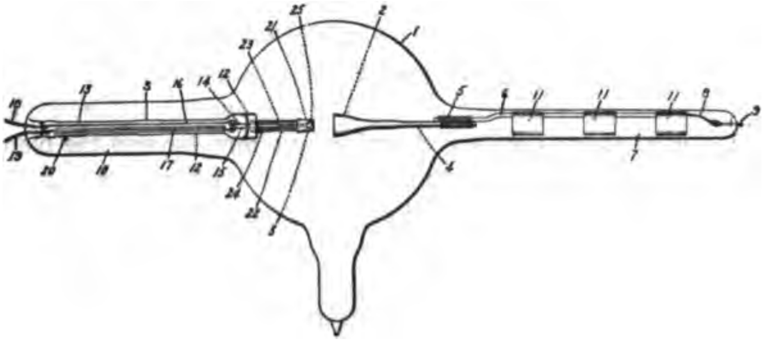

Fig. 1.

Fig. 2 shows an enlarged detail of the cathode and of the front end of the target.

The Cathode.

In the diagrams, 25 is a tungsten filament in the shape of a flat, closely wound spiral. It consists of a wire 0.216 mm. in diameter and 33.4 mm. long with 5½ convolutions, the outermost of which has a diameter of 3.5 mm. It is electrically welded to the ends of two heavy molybdenum wires 14 and 15, to the other extremities of which are welded the two copper wires 16 and 17. These in turn are welded to the platinum wires 18 and 19. The molybdenum wires are sealed directly into a piece of special glass, 12, which has essentially the same temperature coefficient of expansion as molybdenum. This first seal is simply to insure a rigid support for the hot filament, the outer seal being the one relied upon for vacuum tightness. The outer end, 13, of the support tube is of German glass like the bulb itself, and it is therefore necessary to interpose at S a series of intermediate glasses to take care of the difference in expansion coefficients between 12 and 13. The small glass tube, 20, prevents short-circuiting of the copper wires, 16 and 17.

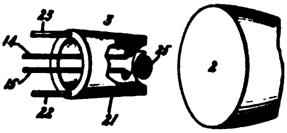

Fig. 2.

The filament is heated by current from a small storage battery which is, electrically, well insulated from the ground.

In the circuit are placed an ammeter and an adjustable rheostat and, by means of the latter, the filament current can be regulated, by very fine steps, from 3 to 5 amperes. Over this current range, the potential drop through the filament varies from 1.8 to 4.6 volts and the filament temperature from 1890 to 2540 degrees absolute.

The Focusing Device.

This consists of a cylindrical tube of molybdenum, 21. It is 6.3 mm. inside diameter and is mounted so as to be concentric with the tungsten filament, and so that its inner end projects 1.0 mm. beyond the plane of the latter. It is supported by the two stout molybdenum wires, 22 and 23, which are sealed into the end of the glass tube, 12. It is metallically connected to one of the filament leads, at 24.

Besides acting as a focusing device, it also prevents any discharge from the back of the heated portion of the cathode.

The Anticathode or Target.

The anticathode or target, 2, which also serves as anode, consists of a single piece of wrought tungsten, having at the end facing the cathode a diameter of 1.9 cm. (Its weight is about 100 gm.) By means of a molybdenum wire, 5, it is firmly bound to the molybdenum support, 6. This support is made up of a rectangular strip and, riveted to this, three split rings, 11, 11, 11, all of molybdenum. The split rings fit snugly in the glass anode arm, 7. They serve the double purpose of properly supporting the anode and of conducting heat away from the rectangular strip and so preventing too much heat flow to the seal of the lead-in-wire, 9.

The Bulb.

This is of German glass and about 18 cm. in diameter.

The Exhaust.

This is as thorough as possible.

For the earlier tubes, mercury pumps were used, with a liquid-air trap between tube and pump to eliminate mercury vapor. The whole tube, while connected to the pump, was in an oven and was heated at intervals to 470° C. Between heating operations the tube was operated with as heavy discharge currents as the condition of its vacuum would permit. For hours the tube would show the characteristics of an ordinary Röntgen tube, and in many cases a several days' application of the above treatment was required to entirely eliminate these characteristics and to realize an essentially pure electron discharge.

The exhaust time has been greatly reduced in two ways. The massive tungsten anode is given a preliminary firing to a very high temperature in a tungsten-tube vacuum furnace.[1] The molybdenum support is also fired, to a somewhat lower temperature, in the same manner. In the second place, a Gaede molecular pump has been substituted for the mercury pumps and, at the same time, a very large and short connection has been adopted between tube and pump.

In the later stages of the exhaust a very heavy discharge current is maintained continuously on the tube for perhaps an hour, the temperature of the bulb being kept from rising too high by the use of a fan.

The pressure in the finished tube is very low, certainly not more than a few hundredths of a micron and probably much less than this.

Connections and Method of Operating.

The tube was connected as shown in the diagram, Fig. 3, in which, *T* is the tube; *B* is a small storage battery; *A* is an ammeter; *R* is an adjustable rheostat which can be controlled from behind the lead screen which shields the operator from the Röntgen rays; *S* is an adjustable spark gap with pointed electrodes, which can also be operated from behind

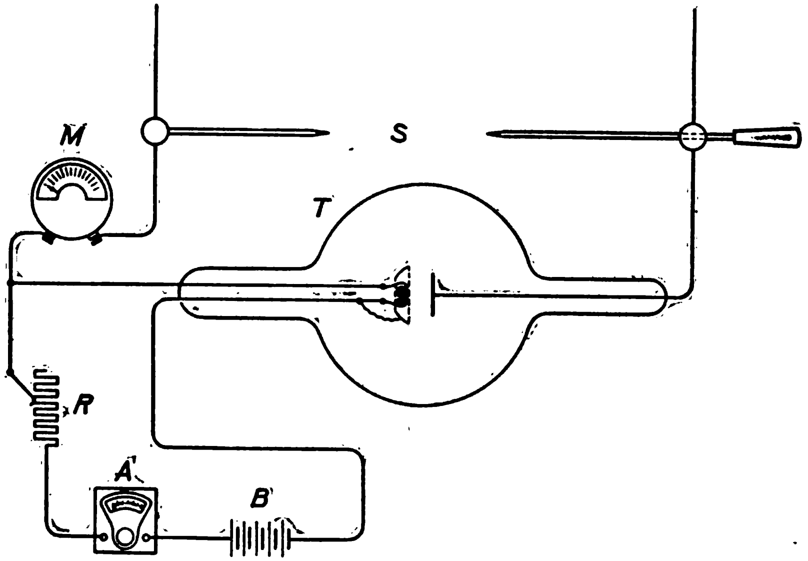

Fig. 3.

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[1] A description of this furnace will be published in the near future. The heating element consists of a tungsten tube 2.5 cm. inside diameter and 30 cm. long. This is fastened in an upright position and, by means of suitable terminals, is connected to a 100 K.W. transformer. The heating element is placed in a water-cooled metal cylinder and the space within connected to a pump which maintains, with the furnace at its highest temperature, a vacuum of a few microns.

the lead screen; and *M* is a milliampere-meter which can be read from behind the screen.

As the high potential is connected to the battery circuit it is necessary that the latter shall be thoroughly insulated from the ground.

As a high potential source, a 10 K.W. Snook machine, made by the Röntgen Apparatus Co., was used. This consists of a rotary converter driven from the direct current end and delivering alternating current at 150 volts and 60 cycles per second to a closed magnetic circuit step-up transformer with oil insulation. From the secondary of this transformer the high voltage current is passed through a mechanical rectifying switch (which is direct-connected to the shaft of the rotary) and the milliampere-meter, *M*, to the tube. The output of the transformer is controlled by a variable resistance in the primary.

Throughout these experiments a fan was kept blowing on the tube. Without this fan, the gas pressures in the tube would be slightly higher, and the discharge currents would be in consequence slightly lower.

§ 5. CHARACTERISTICS.

A. No Discharge Current unless Filament is Heated.

Unless the filament is heated, the tube shows no conductivity in either direction, even with voltages as high as 100,000.

B. Tube Allows Current to Pass in only One Direction.

The tube suppresses any current in the direction which does not make the hot filament cathode. It is therefore capable of rectifying its own current when supplied from an alternating source.

In the case of a focusing tube, however, the use of alternating current will very considerably lower the maximum allowable energy input. For as soon as the target becomes heated at the focal spot to a temperature approximating that of the filament, the tube will cease to completely rectify and, as the temperature of the focal spot rises, will allow more and more current to pass in the wrong direction. This, to be sure, will not cause either a harmful vacuum change or a metallic deposit on the bulb, as it would in the case of the ordinary tube, but it will give rise to needless heating of the bulb where it is bombarded by the cathode rays from the target, and to disturbing Röntgen rays emanating from the glass at this point. In the case of a tube which does not focus, but in which the cathode rays bombard the entire surface of the anode, the allowable energy input which the tube will completely rectify can be increased to any desired amount by simply increasing the surface of the anode.

C. *Discharge Current Determined Primarily by Filament Temperature.*

With a given design, the amount of discharge current which can be passed through the tube is determined primarily by the temperature of the filament, and responds instantly to changes in the same in either direction.

The effect of both temperature and voltage on the discharge current, in the case of tube No. 147, illustrated in Fig. 1, may be seen by referring to Table I., which gives the data on the finished tube after it had been sealed off from the pump. The focal spot was 3 mm. in diameter.

In the table, Column I. gives the length in centimeters of the equivalent spark gap.

Column II. gives the heating current (C) in the filament, expressed in amperes.

Column III. gives the filament temperature (T), expressed in degrees absolute, corresponding to the values of C in Column II. The temperature values were obtained by comparison with a previously calibrated tungsten lamp.

Column IV. gives the discharge current (i) through the tube, in milliamperes.

Column V. gives the calculated values of $(-\log i/\sqrt{T})$ to the base 10.

Column VI. gives calculated values of $(.434/T \times 10^6)$.

To obtain the data in the table, the experimental procedure was as follows: The filament current was first set at a predetermined point. The spark gap was next set, also at a predetermined point. The tube was then excited and the voltage across the tube terminals adjusted (by varying the resistance in the primary circuit of the transformer) until sparks were occasionally jumping across the parallel spark gap. The discharge current value was then read off from the milliammeter.

The filament current was then raised to a second predetermined value. This increased the discharge current and lowered the potential across the tube terminals. The latter was then raised to its original value and and the new discharge current reading was obtained.

In this way the discharge current value, for a given voltage, was brought up by steps to the point where the tube finally began to show signs of instability. The temperature-current series was then repeated with a different voltage.

The values of discharge current and temperature, for each voltage, are plotted in Fig. 4. The different curves are seen to lie very close together, showing that over the range of voltages employed, the magnitude of the discharge current is practically independent of voltage.

This shows that the current in these experiments was always the saturation value.[1]

According to Richardson, the relation between the saturation current flowing from a hot filament and the absolute temperature of the filament, is expressed by the equation $i = a\sqrt{T}e^{-\frac{b}{T}}$, in which i is the current, T is the temperature, and a and b are constants of which the first has to do with the concentration of electrons within the hot body, and the second represents the amount of work required to get the electron through the surface of the metal. e is the base of the Naperian system of logarithms.

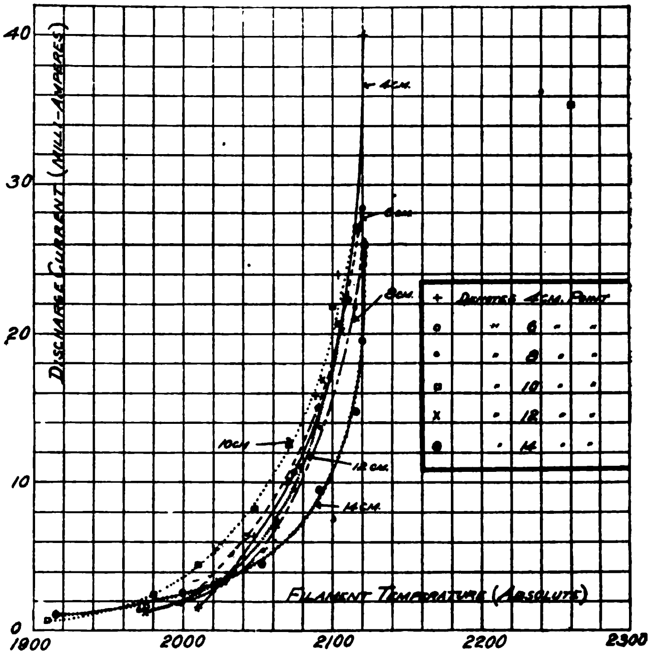

Fig. 4.

Richardson[2] applies this equation to his data by first taking the logarithm, to the base 10, of both sides of the equation, which gives

$$\log i = \log a + \tfrac{1}{2}\log T - \frac{b}{T}(.434)$$

or

$$-\log\frac{i}{\sqrt{T}} = b\,\frac{.434}{T} - \log a,$$

which is the equation of a straight line.

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[1] The two points to the extreme right of the curves correspond to an unstable condition of the tube. The instability disappears instantly upon lowering the filament temperature.

[2] O. W. Richardson, Proc. Camb. Phil. Soc., *11*, p. 293 (1901).

Table I.

I.	II.	III.	IV.	V.	VI.
Equivalent Spark Gap (Cm.).	Filament Current C (Amps.).	Filament Temp. T (Degs. Abs.).	Discharge Current i (Milliamps.).	$-\text{Log}\,\frac{i}{\sqrt{T}}$	$\frac{.434}{T} \times 10^6$
4	3.40	2010	1.7	1.4212	216.1
	3.45	2028	3.5	1.1094	214.1
	3.51	2049	6.4	.4985	212.0
	3.60	2077	11.3	.6056	209.1
	3.66	2088	15.8	.4611	208.0
	3.67	2104	24.0	.2813	206.4
	3.71	2116	27.0	.2313	205.3
	3.73	2121	40.0	.0611	204.8
6	3.29	1976	1.6	1.4438	219.8
	3.43	2020	3.3	1.1341	215.0
	3.52	2053	6.5	.8433	211.5
	3.59	2074	10.6	.6331	209.4
	3.64	2090	15.3	.4753	207.8
	3.70	2110	22.3	.3138	205.8
	3.72	2120	28.3	.2113	204.9
8	3.27	1970	1.6	1.4431	220.4
	3.43	2020	2.9	1.1902	215.0
	3.53	2055	5.7	.9005	211.3
	3.59	2074	9.7	.6716	209.4
	3.64	2090	13.8	.5201	207.8
	3.71	2116	21.8	.3242	205.3
	3.73	2121	26.2	.2449	204.8
	4.07	2240	36.2	.1164	193.9
10	3.09	1909	0.6	1.8411	227.5
	3.31	1980	2.5	1.2504	219.4
	3.40	2010	4.4	1.0081	216.1
	3.50	2046	8.2	.7416	212.3
	3.57	2070	12.6	.5576	209.8
	3.67	2104	20.7	.3455	206.4
	3.65	2096	21.8	.3222	207.2
	3.71	2116	27.0	.2313	205.2
	4.13	2259	35.4	.1279	192.3
12	3.28	1973	1.7	1.4171	220.2
	3.44	2023	3.4	1.1215	214.7
	3.55	2061	7.3	.7937	210.7
	3.57	2070	10.1	.6537	209.8
	3.65	2093	16.9	.4325	207.5
	3.68	2107	22.4	.3116	206.1
	3.68	2107	20.1	.3586	206.1
14	3.11	1917	1.0	1.6413	226.6
	3.36	1998	2.5	1.2624	217.4
	3.52	2053	4.5	1.0030	211.5
	3.64	2090	8.6	.7255	207.8
	3.71	2116	14.7	.4954	205.3
	3.72	2120	19.6	.3708	204.9
	3.73	2121	26.0	.2482	204.8

If then the values of Columns IV. and V. are plotted, they should lie along straight lines, provided conduction in the tube, between the voltage limits used, follows Richardson's Law.

Reference to the plots, Figs. 5 and 6, will show that the points are closely represented by straight lines. By reading off the tangents of the angles which the lines make with the horizontal axis we get the following values of the constant *b*:

Voltage Corresponding to Spark Gap of	Value of *b*.
4 cm.	115,000
6 cm.	93,000
8 cm.	94,000
10 cm.	71,000
12 cm.	76,000
14 cm.	60,000
Average	85,000

These values of *b* are interesting in that they all fall within the range of the values which are just being published by Dr. Langmuir. His values were obtained from an apparatus in which the electrodes were fine tungsten filaments having a total mass perhaps 1/100,000 of that of the target in the above tube. His results show the enormous effect of gas on the value of *b*, and the conclusion can, therefore, be drawn, that very large tungsten masses can be used in a tube without, to any appreciable extent, impairing the vacuum, even though these masses may be heated close to their melting point.

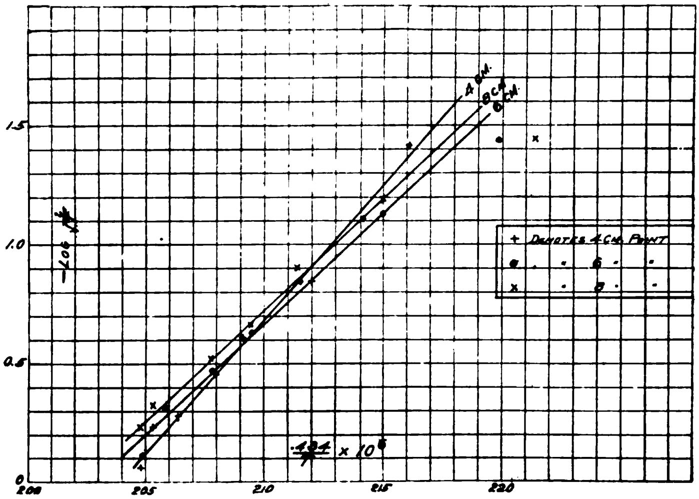

Fig. 5.

If the temperature of the filament is low, only a small number of electrons escape from it and, consequently, only a small discharge current (the saturation current) can be sent through the tube. Increasing the impressed voltage above that needed for this current value causes no further increase in current. It simply increases the velocity of the cathode rays and hence the penetrating power of the Röntgen rays.

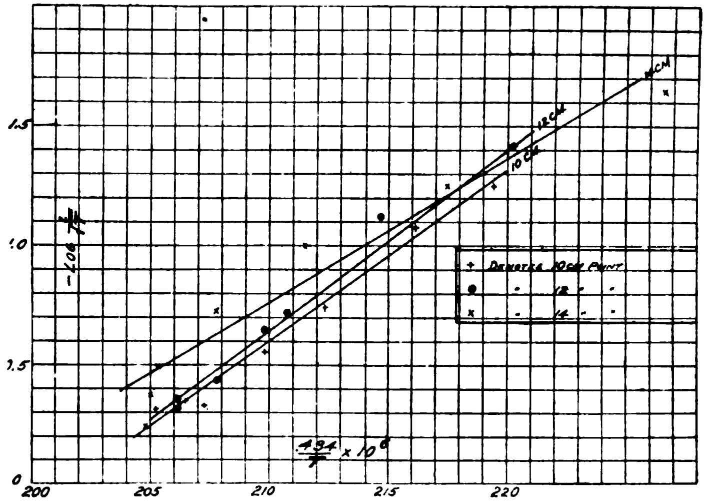

Fig. 6.

At higher filament temperatures there is a current-limiting factor, other than the number of electrons emitted by the hot filament, which plays a dominating part. This factor is the spacial density of negative electricity in front of the cathode, which amounts, in effect, to a back electromotive force. This factor would play a very important rôle at lower voltages; but in the case of the Röntgen ray tube the voltages involved are so high that, in case a suitable design is used, its influence can be entirely avoided, as is shown by the data of Table I.

D. *Penetrating Power of Röntgen Rays Determined by Voltage across Tube Terminals.*

The penetrating power of the Röntgen rays coming from the tube increases with the potential difference between tube terminals.

With the tube excited from a variable potential source, such as the transformer, it did not seem safe to predict that, with the same equivalent spark gap, the rays would show, photographically, the same penetrating power as those from a standard tube. But upon making the experiment, using a Benoist penetrometer,[1] it was found that they did.

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[1] M. L. Benoist, C. R., *134*, 225 (1902).

The experiment was interesting from another point of view in that it showed how readily the new tube could be adapted to a given set of conditions.

An exposure was made first with a standard tube of the ordinary type, and the discharge current and equivalent spark gap were noted. A tube of the new type was then set up in place of the standard. It was but the work of a moment to adjust the new tube to the point where it showed the same discharge current and equivalent spark gap as the standard tube. The radiographs of the penetrometer, made with the two tubes, showed the same penetration number.

E. *Capable of Continuous Operation without Change of Characteristics.*

That the tube may be operated continuously without showing an appreciable change in characteristics is shown by the following experiment on Tube No. 147, illustrated in Fig. 1.

The filament current was set at 4.1 amperes. This gave a discharge current of 25 milliamperes. The impressed voltage was then set at a point where the tube showed a 7 cm. equivalent spark gap.

The tube was then run continuously, with no adjustment of any kind, for 50 minutes. The readings of discharge current and equivalent spark gap, taken every two minutes, are given in Table II.

F. *Sharpness of Focus.*

Sharpness of focus is determined mainly by the design of the tube. If the filament temperature is such that, with the voltage employed, the discharge current does not represent the saturation value, the size of the focal spot will vary with the impressed voltage. But in the tube shown in Fig. 1, over the range of voltages corresponding to an equivalent spark gap ranging from 4 to 14 cm., the focal spot does not vary appreciably in size.

The tube may be made to focus more sharply by increasing the distance between the filament and the front (end facing the target) of the molybdenum tube. This change in design will also affect the temperature-current characteristics of the tube in the direction that a higher filament temperature will be needed for a given discharge current value.

Similarly it may be made to focus less sharply by decreasing the distance between the filament and the front of the focusing device.

All of the observations made are consistent with the idea that focusing is determined by the shape of the equipotential surfaces which may be drawn in the space between cathode and anode, and that the surfaces close to the cathode have the strongly preponderating influence.

TABLE II.

Time.	Discharge Current (Milliamps.).	Equivalent Spark Gap (Cm.).
11:48 A.M.	25	7.0
:50	25	7.0
:52	25	6.9
:54	25	6.5
:56	25	6.5
12:00 P.M.	25	6.7
:02	25	6.9
:04	25	6.5
:06	24	6.4
:08	24	6.5
:10	24	6.5
:12	23	6.6
:14	25	7.0
:16	25	6.8
:18	24	6.8
:20	25	6.9
:23½	23	6.7
:26	23	6.9
:28	25	6.9
:30	25	6.9
:32	25	7.0
:34	24	6.9
:36	25	7.0
:38	24	7.1

Near the cathode, the velocity of the electrons is relatively small, and the direction of their motion will therefore conform closely to the direction of the strong electric force. Near the anode, on the other hand, the velocity of the electrons is so high that the same force acting over the same length of path will produce but little deflection.

G. Fixity of Position of Focal Spot.

The focal spot on the anode does not wander, but remains perfectly fixed in position. This is in sharp contrast to the ordinary Röntgen tube in which the focal spot does move about, and often so rapidly as to be noticeable even during the shortest radiographic exposures.[1] The effect of movement of the focal spot is, of course, to cause in the radiograph or on the screen, a blurring of all lines except those parallel to the direction of motion. In the earlier stages of exhaustion, while the new tube is being operated with a relatively poor vacuum, the focal spot may dance about, but as the electrodes and the glass become freer from gas the motility of the focal spot decreases and finally disappears completely. Its disappearance goes hand in hand with the disappearance of fluorescence of the glass, discussed in section *J*. Movement of the focal spot appears to be due to the action of positive ions in disturbing the distribution of static charge on the glass walls of the tube.

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[1] See Dr. Pfähler, Fortschritte auf dem Gebiete der Röntgenstrahlen, *18*, pp. 340–343 (1911–1912).

H. Tube not Sensitive to Considerable Changes in Gas Pressure.

The gas pressure within the tube is so low that it can increase severalfold, and apparently decrease without limit, without appreciably affecting the other characteristics.

The slight effect of pressure change may be seen from the following experiment:

While one of the tubes was being continuously operated on the pump, the pressure, as indicated by a McLeod gage, decreased from 0.113 to 0.035 micron.[1] The discharge current passing through the tube remained constant at 3.1 milliamperes, while the parallel spark gap backed up by the tube changed only from 7.9 to 8.6 cm. A corresponding pressure change in the case of an ordinary Röntgen tube would bring about an enormous change in current and voltage.

I. Capable of Continuous Operation with High Energy Input.

Owing to the fact that the tungsten target can run at such a high temperature, large amounts of energy can be continuously radiated.

J. No Fluorescence of Glass.

When operating properly the tube shows no fluorescence of the glass at any point. Corresponding to this, there is an absence of the usual strong local heating of the anterior hemisphere. The absence of fluorescence and of local heating seem to point to the fact that there is no bombardment of the glass by secondary cathode rays sent out from the target. This is in striking contradistinction to what takes place in an ordinary Röntgen tube, where, in the case of a platinum target, it has been found that there are about three-fourths as many electrons leaving the target, and going to the glass, as secondary cathode rays, as there are bombarding it, in the form of primary cathode rays. This elimination of secondary cathode ray bombardment prevents the production of a large part of the useless and disturbing Röntgen rays which emanate from the glass in the case of the ordinary tube.

The absence of bombardment of the glass is of interest both theoretically and practically. Other explanations of the lack of fluorescence suggested themselves at first. A plausible hypothesis was that bombardment took place, but that the surface of the glass was much freer from gas than it is in the ordinary tube and that this accounted for the lack of fluorescence. But the fact that fluorescence appears so suddenly when a trace of gas is evolved, coupled with the fact that such fluorescence may appear in streaks and that these may rapidly change their location, seems to disprove the hypothesis. It also seemed possible at first that the fluorescence might be there, but that it could not be seen because of the strong light emission from both filament and target. But this hypothesis is disproved by the fact that with filament and target at their highest temperatures, fluorescence becomes suddenly strongly visible whenever gas is liberated.

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[1] In the light of later experiments it seems doubtful whether a further pressure decrease, no matter how great, would have appreciably affected the tube characteristics.

The simple explanation appears to be based upon the fact that the large number of positive ions present in an ordinary Röntgen tube is here lacking. The inner surface of the glass becomes strongly negatively charged, when the tube is first operated, and, not being able to attract an appreciable number of positive ions, remains so. The presence of this negative charge upon the glass prevents further electrons, either in the shape of primary or secondary cathode rays, from going there.

K. *Identity of Starting and Running Voltage.*

The starting, or break-down, voltage of the tube is the same as the running voltage. This is very different from the state of affairs in the ordinary tube in which the break-down voltage is much higher than the running voltage.[1] The difference is to be explained as follows: In the ordinary tube the number of ions present when the circuit is closed is exceedingly small, being only that due to natural ionization causes, such as radioactive matter in the surroundings. After the discharge circuit is closed, the number of ions increases, by collision, very rapidly, and the voltage across the tube terminals falls in consequence. In the case of the new tube, on the other hand, the full supply of electrons is there the instant the discharge circuit is closed, and even before this, and the available number is not changed by the discharge current.

L. *Permits of Realization of Homogeneous Bundle of Primary Röntgen Rays.*

The tube must permit of the realization of a strong homogeneous bundle of primary Röntgen rays of any desired penetrating power. For this purpose it should clearly be excited from a source of constant potential. The result should be attained even though the discharge is intermittent.[1]

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[1] See Dessauer, l. c.

M. No Heating of Cathode by Discharge Current and no Evidence of Cathodic Disintegration.

An earlier experiment showed that when a tube is made up with two similar concave tungsten electrodes, symmetrically located in the tube, and operated on direct current at an ordinary Röntgen tube vacuum, the heating effect at the cathode is as strong as that at the anode. Furthermore, the heat evolution at the cathode is as strongly localized as it is at the anode. In fact, it is impossible, when the tube is operating, to tell, by looking at it, which of the white hot electrodes is functioning as anode and which as cathode. There is a very rapid blackening of the bulb in such a tube, the material of the deposit coming evidently from the cathode, which shows a deep and sharply defined cavity at the point of local heating. The simple explanation seems to be that the cathode is bombarded by positive ions and that the emission of the electrons which constitute the cathode ray stream is due to this bombardment. So, also, the heating effect and the cathodic disintegration.

At the higher vacuum and with the relatively gas-free electrodes of the new tube there is no evidence of any bombardment of the cathode. In the earlier stages of gas removal, when a discharge can be made to pass through the tube without the heating current in the filament, the latter is seen to be strongly locally heated by the discharge current, as from bombardment by positive ions. But when the exhaustion has been completed and the tube is operated with the cathode hot, a voltmeter and ammeter in the filament circuit show no change even when a very heavy discharge is sent through the tube. Positive ion bombardment, if it existed to an appreciable extent, would raise the temperature and, hence, the resistance of the tungsten filament and would therefore be indicated by the instruments. If it were very local and considerable, it would be further indicated by a melting through of the filament at the point in question. The resistance change and local disintegration of the filament have been observed in only those cases where the vacuum, as shown by other effects, such as fluorescence of the glass, has been poor.

Disintegration of the cathode would also manifest itself in blackening of the bulb. Even after running for several hours, the deposit on the bulb is very slight, and what there is may well be entirely accounted for by vaporization of tungsten at the focal spot on the target.

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[1] For fluoroscopic work with the ordinary tube, it seems preferable to use an interrupted discharge so as to reduce heating of the tube and danger to patient and operator. The phosphorescence of the fluoroscopic screen makes possible frequent interruptions without appreciable loss of light.

N. The Target the Factor Limiting Allowable Energy Input.

There is one limitation with the new tube. With a sharp focusing tube and above a certain energy input the tube resistance is unstable, dropping suddenly to perhaps a small fraction of its original value, returning instantly to the old value however upon stopping the discharge or upon lowering it to the limiting value. The cause of this phenomenon appears to be as follows:

With a very high energy input and sharp focusing, the surface of the target melts at the focal spot and volatilizes. Owing to the fact that this tungsten vapor is produced at the focal spot, all of the primary cathode rays pass through it and, by collision, ionize it. This of course decreases the tube resistance. The larger the focal spot the greater is the limiting current. The design of the target also has a great deal to do with the limiting current value, as the face of a thin target is vaporized with a much lower energy input than a relatively thick one. For very short excitation of the tube, the limiting energy input is somewhat larger than for longer periods; but an input which can be carried for a few seconds can be carried indefinitely.

The effect of substituting any other single refractory metal for the tungsten of the target will be to lower the maximum allowable energy input. For the essential properties of a target material are: high density, high melting point, high heat conductivity, and low vapor pressure. Tungsten has a higher melting point and lower vapor pressure than any other metal. Its nearest competitor in point of refractoriness, tantalum, has only about one third of the heat conductivity. Molybdenum and iridium have vapor pressures altogether too high to entitle them to consideration, even if their melting points made them otherwise competitors. Osmium has only about one half of the heat conductivity of tungsten.

The ordinary copper-backed tungsten target would be very difficult to exhaust sufficiently. Otherwise its use might be desirable for certain classes of work, as it would raise the maximum allowable instantaneous energy input.

§ 6. DANGER CONNECTED WITH USE OF TUBE.

There has been in the old tube a certain element of safety in that it could not be run continuously with a very heavy energy input. The new tube, even when focusing sharply, can be operated, for example, on a 7 cm. parallel spark gap with currents as high as 25 milliamperes for hours at a time, and without the slightest attention.

For most purposes, other than diagnostic or radiographic work, there is no advantage in having the tube focus. In case it does not, the above-mentioned energy input limitation falls away and the tube can apparently be designed for any energy input whatsoever. This will permit, in this field, of the use of much greater Röntgen ray intensities than have heretofore been realized.

In the light of the above, it will be seen that the precautions which have been shown by years of experience to be sufficient for work with the old tube are not necessarily sufficient for the user of the new one.

§ 7. SUMMARY.

In the foregoing, a new and powerful Röntgen ray tube has been described. It differs in principle from the ordinary type in that the discharge current is purely thermionic in character. Both the tube and the electrodes are as thoroughly freed from gas as possible, and all of the characteristics seem to indicate that positive ions play no appreciable rôle.

The tube allows current to pass in only one direction and can therefore be operated from either direct or alternating current.

The intensity and the penetrating power of the Röntgen rays produced are both under the complete control of the operator, and each can be instantly increased or decreased independently of the other.

The tube can be operated continuously for hours, with either high or low discharge currents, without showing an appreciable change in either the intensity or the penetrating power of the resulting radiations.

The tube in operation shows no fluorescence of the glass and no local heating of the anterior hemisphere.

The starting and running voltage are the same.

The tube permits of the realization of intense homogeneous primary Röntgen rays of any desired penetrating power.

An article bearing especially upon the application of the new tube to radiographic and diagnostic and to therapeutic purposes will appear shortly in one of the Röntgen ray journals.

It is a pleasure to me, in closing, to express my appreciation of the services of Mr. Leonard Dempster, who has assisted me throughout this work.

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THE CHANGE IN THE ELASTICITY OF A COPPER WIRE WITH CURRENT AND EXTERNAL HEATING.

BY H. L. DODGE.

THE present investigation consists of determinations of Young's modulus of a specimen of copper wire at various temperatures between 20° C. and 150° C. with the object of ascertaining whether or not heating by an electric current has any effect other than that caused by the accompanying increase of temperature, and also to learn certain facts regarding the temperature effect itself, concerning which there seems to be considerable doubt.

PREVIOUS RESULTS UPON THE EFFECT OF CURRENT HEATING.

Wertheim[1] reported a decrease in Young's modulus caused by current and believed this decrease to be independent of any temperature effect, a conclusion not sufficiently justified as he assumed the heating effect of the current negligible. Edlund[2] made allowance for the temperature effect, and concluded that current, except for the accompanying temperature change, does not affect Young's modulus. Streintz[3] made observations of the torsion modulus at room temperature and at 55.5° C. The following figures represent the percentage change of elasticity caused by the current, correction being made for the temperature effect: Brass (*a*), − 5.9; (*b*), + 12.8; copper, 0.0; silver, + 3.9; iron, + 3.1; steel, − 12.2. Mebius[4] found the effect due to current in the case of steel, iron, brass, and silver rods to be extremely small. Miss Noyes[5] studied steel, silver, and copper wires and found that the current heating caused a uniform decrease in Young's modulus which could be entirely accounted for as a temperature effect. Walker[6] employed the same experimental methods as Miss Noyes, but found very irregular changes with steel, soft iron, platinum, and copper, which could not be accounted for by temperature and which differed greatly with increasing and decreasing current. A survey of previous work leaves a serious doubt as to the effect of current heating, and this doubt a critical study serves to increase.

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[1] Ann. de Chim. et de Phys., 12, 610, 1844.

[2] Annal. d. Phys., 129, 15, 1866; 131, 337, 1867.

[3] Annal. d. Phys., 150, 368, 1873.

[4] Oefvers. af k. Vet. Akad. Forhandl., 681, 1887; Beibl. 12, 678.

[5] PHYS. REV., 2, 279, 1895; 3, 433, 1896.

[6] Proc. Roy. Soc. Edin., 27, 343, 1907.

PREVIOUS RESULTS UPON THE CHANGE OF YOUNG'S MODULUS WITH TEMPERATURE.

The investigations that have been carried on to determine the change of Young's modulus with temperature are so extensive that the results with copper only can be considered. These are however representative of the results for other metals. Shakespeare[1] has found a decrease of Young's modulus for copper of 3.6 per cent. on heating from 13° C. to 100° C. Miss Noyes[2] made observations at various temperatures up to 150° C. and reports a uniform decrease of the modulus of 0.13 per cent. and 0.07 per cent. per degree for two samples of wire. Gray, Blyth, and Dunlop[3] also were able to make observations at intermediate temperatures up to 100° C. They also report a uniform decrease, which for two samples was 0.015 per cent. and 0.04 per cent. per degree respectively. On the other hand Slotte's[4] observations at intervals over a range of 10° C. to 70° C. upon two samples of copper wire showed a decrease of Young's modulus with increase of temperature which was not uniform but became less rapid with one sample and more rapid with the other as the temperature increased. An increasing rate of change is also indicated by the results of Wertheim[5] at 15° C., 100° C., and at 200° C., the change being much greater for the upper interval. In this connection the work of Pisati,[6] Kohlrausch and Loomis,[7] and of Slotte[8] upon the torsion modulus is of interest. They found the rate of decrease of the modulus greater as the temperature was raised. This is suggestive as it is highly probable that the general nature of the elastic changes is similar for the two moduli. These results leave no doubt that increase of temperature causes a decrease of Young's modulus, but there is no conclusive evidence as to the exact nature of the decrease.

SCOPE OF WORK.

In view of the facts which have been cited it was decided to attempt an investigation of the effect of current upon Young's modulus, accompanied by a parallel investigation of the temperature change produced by an external source of heat. Examination of the previous work led me to believe that the desideratum was not a hastily made series of observations upon a number of metals but rather thorough and extended observations upon a single metal. Consequently this report is confined to results with copper although work is under way with other metals. A review of the literature made clear that the causes of inaccurate results in the past have been chiefly a lack of mechanical perfection in the apparatus and insufficient attention to the distribution of temperature. In none of the work upon the effect of current has there been any knowledge of the differences in temperature along the wire or any effective attempt made to secure a uniform distribution. The apparent crudity of the apparatus that is here described is the result of an attempt to keep every part of the apparatus as simple as possible and to refrain from unwarranted refinements. Each source of error has been considered in relation to the others and the effectiveness of the apparatus is best judged from the consistency of the results that have been obtained.

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[1] Phil. Mag., 47, 539, 1899.

[2] Loc. cit.

[3] Proc. Roy. Soc., 67, 180, 1900.

[4] Acta Soc. Scien. Fennicæ, Vol. 26, 1899.

[5] Loc. cit.

[6] Nuovo Cimento, 4, 152, 1878; 5, 34, 135, 1879.

[7] Annal. d. Phys., 141, 481, 1871.

[8] Acta Soc. Scien. Fennicæ, Vol. 35, 1908.

Description of the Apparatus.

In order to prevent convection currents and consequent non-uniformity of heating necessarily accompanying vertical suspension the wire was mounted horizontally. The mechanical features of the apparatus (Fig. 1) may be considered independently of the heating box. The wire is suspended between a bar (b) and a pulley (p) which are in turn supported by a heavy cast iron base, bolted to the carriage of the dividing engine. The wire is stretched by the weights W_1 and W_2. Current is led in at the points (d) through the mercury cups (c), the wire being insulated at (a) and at (b). Three copper-constantan thermo-couples (t) of No. 36 wire are for temperature measurements. The weight W_1 is kept upon the wire continually and is heavy enough to stretch the wire almost straight. The weight W_2 is added gradually and without jar by a simple

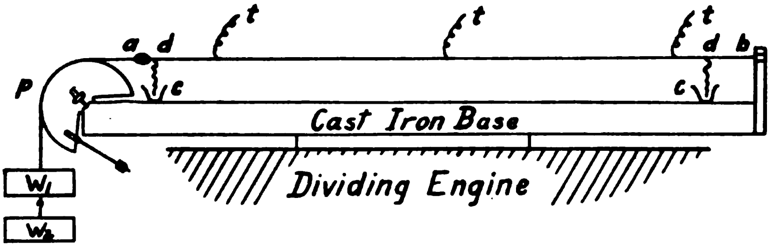

Fig. 1.

The apparatus, showing method of suspending the test specimen.

apparatus operated by a foot lever. The elongation of the wire is measured with two micrometer microscopes attached to the bed of the dividing engine. These are focused upon bright scratches on the wire, made visible by incandescent lamps.

The heating apparatus (Fig. 2), although supported by the cast-iron base, is mechanically entirely independent of the wire. It must not only furnish a means of heating the wire externally but also must retain the heat when the current is passed through the wire itself. The base (*o*), bottom piece (*s*), and back (*v*) are covered with asbestos and fastened together. The asbestos-covered front (*h*), which has two windows of mica (*m*) for observing the wire, and the glass cover (*n*) are held together by clamps easily removed. The glass tubes (*k*) are large enough to give sufficient clearance to the wire (*w*) but small enough to prevent convection or other air currents. Zigzagging back and forth across the bottom piece (*s*) is a heating wire of German silver through which a current can be sent. This heating box proved to be one of the three important features of the apparatus and its simple form in no way indicates the difficulty of securing a reasonably even temperature distribution. This fact is very suggestive in connection with the results of former investigations in which average temperature only was known, there being no information concerning the temperature distribution. The use of thermo-couples which could be slipped to different portions of the wire revealed surprising inequalities of temperature. Even after uniformity of heating had been secured with the external source it was necessary to still further alter the box before a satisfactory distribution could be obtained with internal or current heating. At the highest temperature employed the maximum variation of temperature over the portion of the wire under observation was less than 15° C.

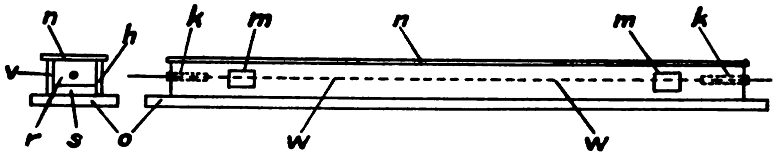

Fig. 2.
Heating box surrounding the test specimen.

A second feature of importance is the free suspension of the wire. The possibility of error due to contact of the wire with rigid portions of the apparatus is eliminated by permitting it to touch nothing except the thermo-couples which are of fine flexible wire. Consequently the specimen hangs freely in the form of a flat catenary. The elongation caused by the straightening of the catenary on the application of the additional stretching weight is negligible, being about 1/100 of the smallest reading of the micrometer microscope. The third feature is also mechanical. It is the pulley which changes the direction of the applied force, which must be transmitted without gain or loss resulting from friction or change of leverage. Fig. 3 shows its construction and suggests the method of centering the axis. The pulley was tested at different positions at various times during the progress of the work and found to introduce no appreciable error.

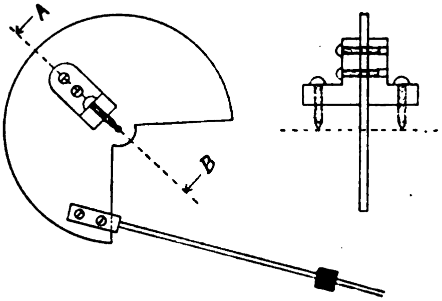

Fig. 3.
Side view of pulley and section along *A–B*.

Method of Determining Temperature of Specimen.

When the wire is heated by the external source it is of uniform temperature throughout its cross section and of the same temperature as the surrounding air. Under these conditions the thermo-couples which have already been mentioned are a perfectly satisfactory means of measuring its temperature. In the case of internal or current heating there is an increase of temperature toward the center, resulting in a number of effects, change of resistance, thermal conductivity, etc., each of which has its influence upon the current distribution and in turn upon the temperature distribution. The average temperature of the wire is of course a function of the surface temperature and of the current, but for evident reasons the thermo-couples do not give the surface temperature of the wire when the wire itself is the source of heat.

Measurement of temperature by change of length caused by thermal expansion has proved to be the most accurate and convenient method. Blondlot[1] has shown conclusively for several pieces of brass and one of German silver that current has no direct effect upon the dimensions of a metal carrying a current. This has also been shown by Righi[1] for four wires whose composition is not given. There is no reason to believe that copper should be peculiar in showing this effect. In fact our own experience and the persistency with which our results for Young's modulus at any temperature as determined by this method remain the same, no matter what may be the source of heat, is in itself proof that current has no direct effect upon the length of the wire. In using change of length as an indication of temperature account must be taken of the change caused indirectly by the effect of temperature upon Young's modulus. Thermo-couple readings and length observations were taken for all work with external heating. With internal heating length observations were made and the temperature determined by comparison with the other results. The thermo-couples were connected to a sensitive Siemens and Halske galvanometer by a three-way switch and were calibrated by direct comparison with an accurate thermometer.

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[1] Journal de Phys., [1], 8, 122, 1879.

With current heating the central portions of the wire tend to lengthen more than the outer portions which are at a lower temperature and it is assumed that the actual lengthening so averages this effect as to be an indication of the average temperature. It is also worthy of notice that the contribution to Young's modulus will be different for the different portions, the value observed being an average of the moduli of the various circular layers making up the cross section of the wire. There is of course a similar averaging of temperature and modulus along the length of the wire.

NATURE OF THE TESTS.

Three sections of commercial copper wire were tested, all from the same piece obtained from the Driver-Harris Wire Co., Harrison, N. J. The purity of the specimen was determined electrolytically, with results of 99.88 per cent. and 99.92 per cent. As the second was the more accurate we may take 99.91 ± .01 as the purity of the specimen. There was no trace of either silver, lead, or iron. The coefficient of linear expansion was .0000169. Specimen No. 2 was 0.81 mm. in diameter. The portion under observation was 50.7 cm. long. The other samples were of similar dimensions. A weight of 2,109 grams was kept upon the wires continually. The modulus was determined by measuring the elongation produced by an additional weight of 2,252 grams. The elongation was observed with a microscope, the micrometer head of which can be read to 1/50 revolution, corresponding to .00093 mm. stretch. At room temperature the stretch amounted to about .02 mm.

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[1] Nuovo Cimento, [3], 7, 116, 1880.

Currents as high as 15 amperes were used. The accuracy of the work is of a high degree. The error in the determination of Young's modulus is about 1 per cent. A greater accuracy may prove desirable if small peculiar effects appear with other metals, but the present apparatus is sufficiently accurate to determine the general nature of the changes in the modulus.

Each determination of Young's modulus as represented by a point on the curves or a value in the tables is the result of ten or more separate measurements taken so as to eliminate any error caused by a slight drift in temperature. Generally a half hour or more was required for the temperature to reach a sufficiently steady state. After the preliminary work the greater part of the observations consisted of series of determinations with increasing or decreasing temperature over a range of 20° C. to 150° C.

PRELIMINARY TESTS.

The possible ways in which current may affect elasticity are so numerous that a determination of Young's modulus at a given temperature is of no value unless interpreted in connection with the whole thermal history of the wire. Since the essential part of this investigation is the comparison of observations taken under as nearly similar thermal conditions as possible, except for the difference in time and in the source of heat, an elimination as far as possible of any other than pure temperature effects is desirable. If this is impossible a thorough understanding of the nature of the other effects is essential. In order to eliminate the well-known permanent changes accompanying extreme temperatures the treatment of the wire after its first heating and stretching was confined to a temperature range of 20° C. to 150° C. In order to find out how consistent was its behavior within this range and under the various conditions of treatment a great deal of preliminary work was necessary. This showed that there are no sudden changes in the elastic state of the wire, that the rapidity of heating and cooling had little if any effect upon the changes in elasticity, and that the length of time the wire was held at a given temperature had no great effect. As explained later, permanent or history effects were found, but for any series of readings these changes were insignificant, the value of Young's modulus returning at the close of any day's observations to practically its original value.

That history effects could be eliminated and the elasticity of the wire made independent of treatment and a function of temperature only is illustrated in Fig. 4, Series 5. Observation 15 is almost identical with 8, and 16 and 17 are nearly the same as the first observations, although the wire had meantime been heated and cooled twice.

In order to learn whether or not at any given temperature the value of Young's modulus is dependent upon the manner of heating, the observations of Table I. were made. The shifting from one method of heating to another was done without permitting much alteration in the temperature of the wire.

TABLE I.

Showing Constancy of Young's Modulus under Different Conditions of Heating, Temperature Remaining the Same.

Method of Heating.	Variation in Length, Mm.	Variation in Stretch, Mm.
12.8 amperes, alternating current	.0000	.0000
12.8 amperes, direct current	.0065	.0009
External, direct current	.0059	.0009
External, alternating current	.0032	.0014
12.2 amperes, direct current	.0018	.0009

The greatest variation in length is .0065 mm. or 0.14 revolution of the micrometer head. This corresponds to a temperature variation of less than one degree Centigrade. The greatest variation in stretch is .0014 mm. This corresponds to only 0.03 revolution and is about the experimental error. These results show clearly that at this temperature, which was approximately 110° C., the stretch modulus is independent of the source of heat. These preliminary investigations and others which need not be described showed the behavior of copper to be very consistent and are the justification for the taking of more extended series of observations and the comparison of results secured at different times.

TESTS UPON SPECIMEN NO. 2.

After specimen No. 2 was placed in the apparatus it was heated to a high temperature and stretched to remove the kinks. Afterward it was never heated above 150° C. The four series of readings composing Fig. 4 were taken after the wire had been heated by both methods a total of about 50 hours and after about 500 applications of the stretching weight. If such a thing were possible as a state in which all changes in elasticity, except those caused by temperature could be eliminated, this treatment should have secured the result.

As far as possible the figures have been made self-explanatory. Certain additional information which is characteristic of all the work is given in Tables II. and III. Series 4 shows a series of observations in which the heating was entirely external. In this as well as in the other three series of Fig. 4 dotted points represent observations taken while the

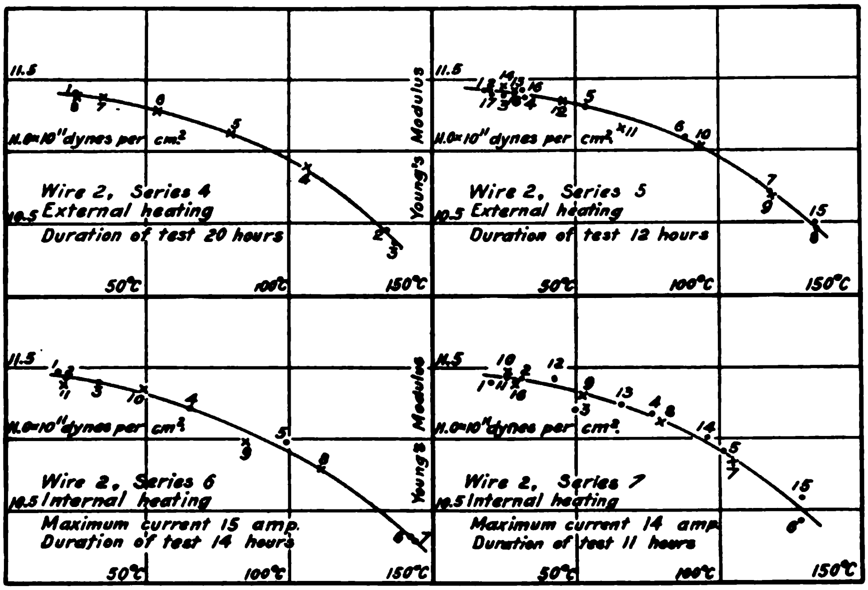

Fig. 4.

Results of tests upon specimen No. 2, showing effect of internal and external heating.

TABLE II.

Data for Series 5, Wire 2, External Heating.

Obs. No.	Time.	Temp.	Stretch (Revs. of Micr. Screw).	Young's Modulus × 10^{-11} Dynes per Cm².
1	9:00 A.M.	18° C.	4.08	11.46
2	9:30	20	4.08	11.46
3	10:05	25	4.10	11.42
4	10:30	33	4.11	11.40
5	11:05	54	4.13	11.33
6	11:50	88	4.205	11.11
7	1:00 P.M.	118	4.35	10.73
8	2:00	135	4.47	10.48
9	2:45	119	4.365	10.70
10	3:15	94	4.24	11.05
11	4:10	67	4.19	11.18
12	4:40	46	4.12	11.38
13		28	4.09	11.44
14	6:00	25	4.075	11.48
15	7:15	134	4.45	10.52
16	8:00	32	4.085	11.45
17	8:45	21	4.10	11.42
18	9:30	28	4.09	11.44

TABLE III.

Data for Series 7, Wire 2, Internal Heating.

Obs. No.	Time.	Temp.	Current, Amperes.	Stretch (Revs. of Micr. Screw).	Young's Modulus $\times 10^{-11}$ Dynes per Cm².
1	10:30 P.M.	21° C.	0.0	4.10	11.42
2	11:15 A.M.	32	3.8	4.085	11.45
3	11:50	50	7.0	4.165	11.22
4	1:05 P.M.	77	9.8	4.18	11.20
5	1:30	102	12.0	4.28	10.93
6	2:30	128	14.1	4.49	10.43
7	3:05	105	11.9	4.31	10.85
8	3:50	80	9.5	4.20	11.13
9	4:20	53	6.8	4.13	11.33
10	5:10	27	0.0	4.07	11.50
11	6:30	27	0.0	4.08	11.46
12	7:25	43	5.0	4.09	11.44
13	8:00	66	8.0	4.15	11.26
14	8:45	97	11.2	4.245	11.02
15	9:15	129	13.9	4.42	10.60
16	9:40	28	0.0	4.10	11.42

temperature was being raised by steps and the crossed points those when the temperature was being lowered. Particular attention is called to points 2 and 3, the second of which was taken after the temperature had been maintained for twelve hours. They show that the length of time the wire was kept at the high temperature had no effect upon its elasticity. The proximity of points 8 and 1 shows the elimination of history effects and permanent changes.

Two days later Series 5 was secured, which yields results identical with those of Series 4, showing that the work of one day can be repeated at a later time. Further proof of the absence of history effects is afforded by the positions of points 14, 15, 16, 17, and 18 relative to observations taken at earlier times at the same temperatures. The fact that points 5, 6, and 7 taken with increasing temperature fall on the same curve as points 9, 10, and 12 taken with decreasing temperature shows the absence of any hysteresis effects.

Series 6 was taken three days later, followed the next day by Series 7. The procedure was the same as before except for the difference in the manner of heating. In Series 4 and 5 the wire was heated externally by means of the heating wire on the bottom of the box enclosing it. In Series 6 and 7 the wire was heated by an electric current in the wire itself. The results of Series 6 and 7 show the absence of hysteresis effects and the elimination of history effects the same as with external heating. The fact that the variation of the curves forming Fig. 4 is less than would be expected from the experimental error shows that one is justified in taking these results as an indication of temperature effect alone and is justified in comparing the results of different days with different methods of heating.

Tests upon Specimen No. 3.

A third sample of the same wire was next placed in the apparatus in order to confirm the results obtained with the former specimen, to attempt still other variations in the thermal treatment and to secures the complete elastic history of a specimen. The results are given in Figs. 5, 6, and 7. Upon these curves appear every observation that was made with the third specimen, not one having been discarded.

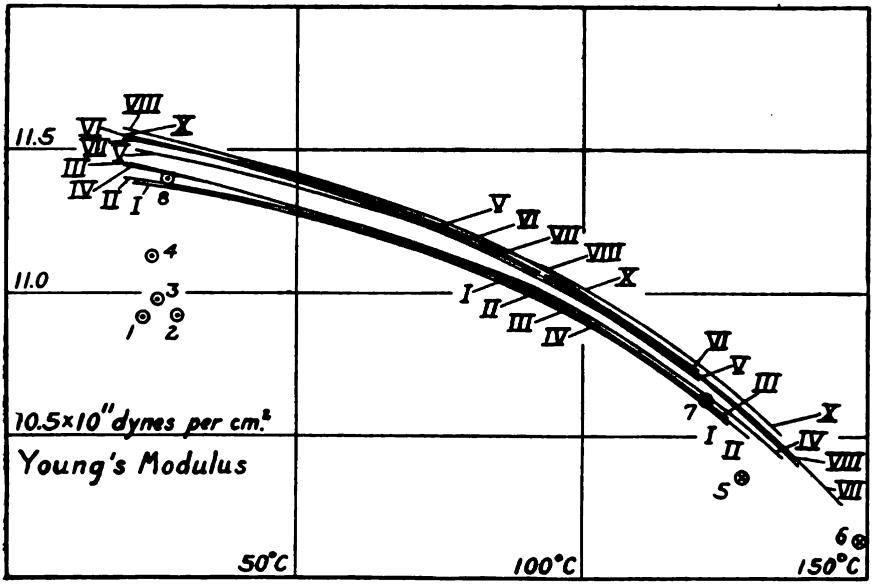

Fig. 5.

Complete elastic history of specimen No. 3. The curves are those of Figs. 6 and 7, the Roman numerals corresponding to the series numbers.

First Changes in Elasticity.—The specimen was made as free from kinks as possible and placed in the apparatus. Observation 1, Fig. 5, was at room temperature. The wire was then heated externally to about 125° C. and cooled. Observation 2 shows no change. Heating by 17 amperes current to about the same temperature brought a slight increase in the modulus as indicated by observation 3. There was very little increase in length during this treatment, as the additional weight was not applied at high temperatures.

It was anticipated that continued application of the additional weight while the wire was hot would remove any kinks in the wire, cause an increase in length and a change in the modulus. The wire was heated by 17 amperes current and the weight applied a number of times. On

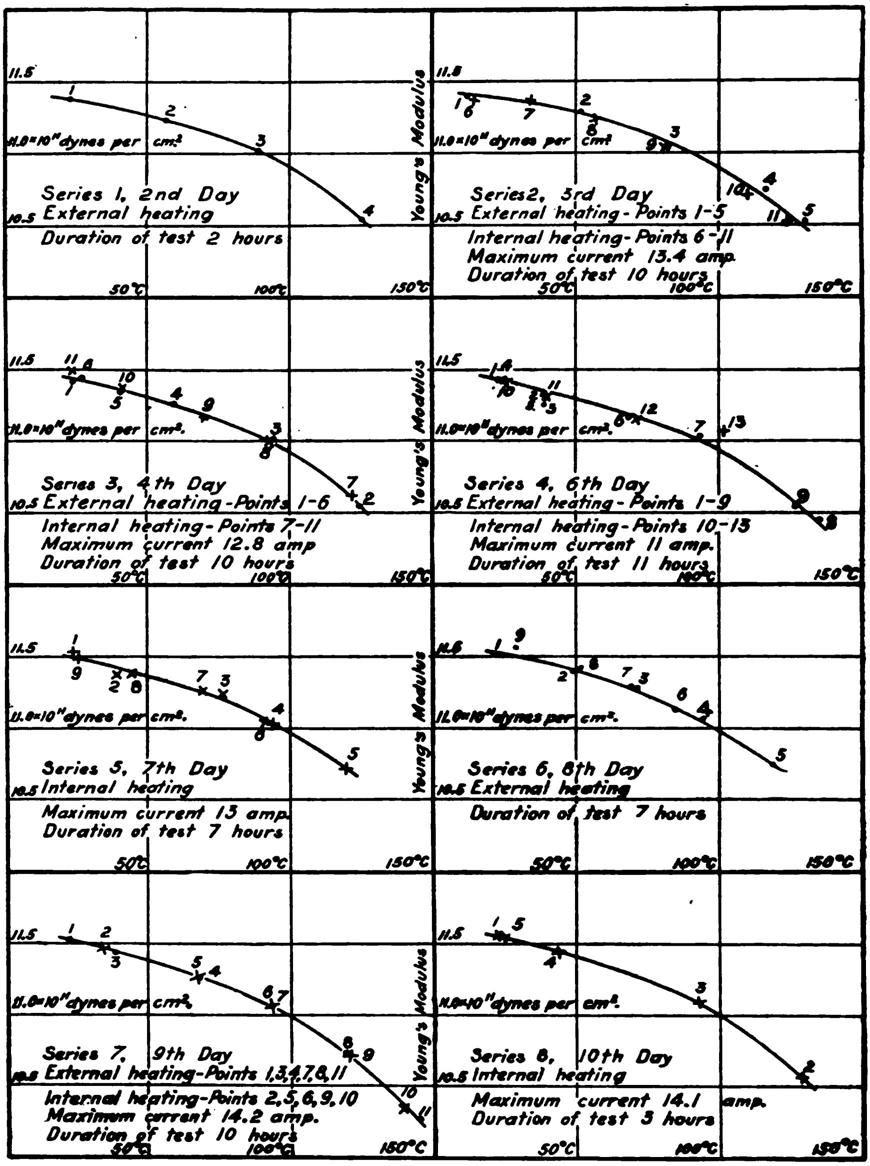

Fig. 6.

Results of tests upon specimen No. 3 with different thermal treatment, showing history effect, change of Young's modulus with temperature, and absence of any effect peculiar to current heating.

cooling an increase of length of about 0.2 mm. was found and an increase of Young's modulus as indicated by observation 4. The wire was again heated to 125° C. and Young's modulus measured at this temperature, resulting in observation 5. The temperature was then increased to about 150° C. and the additional weight applied about thirty times, resulting in observation 6. Cooling to 122° C. gave observation 7, and to 28° C., observation 8. It was believed that a sufficiently steady state had been secured to justify the trial of a series of readings and a comparison of points 6, 7, and 8 with reference to later observations shows this to have been the case. It is highly probable that the increase in Young's modulus due to this particular treatment was caused as much by the mechanical stretching and straightening of the wire as by the thermal treatment, although the latter was undoubtedly essential to the securing of the steady state.

Discussion of Fig. 6.—Following the work just described came eight days of testing under a variety of conditions. Fig. 6 shows the results and has been made practically self explanatory. The order in which the observations at the different temperatures were taken and the manner of heating were varied in a number of ways in order to catch any possible changes caused by treatment. Series 1 is with external heating, increasing temperature. Series 2, first part, was taken in exactly the same manner and the results show that for external heating a sufficiently steady state had been reached so that only small permanent changes were to be anticipated. The second part of Series 2 was taken in exactly the same manner except for the change in the manner of heating, the external heating having been changed to internal by means of the current. No difference is observed. The following day a series was taken in a similar way except that the observations were made with decreasing temperature. The nature of the temperature change remains the same and a slight permanent increase appears.

In Series 4 the systematic heating and cooling over the whole temperature range was not followed, but no peculiar effects were observed. During the following night the wire lay unstretched and it is possible that this had some influence in causing the permanent increase of elasticity observed the next day. Series 5 is the result of heating and cooling with internal heating and Series 6 is for the same treatment with external heating. No hysteresis effect appears nor does there appear any difference due to method of heating.

Discussion of Series 7.—Series 7 is the most interesting single set of observations, and was taken in order to compare the two methods of heating without permitting the elapse of several hours or allowing an appreciable change of temperature. At each temperature at which observations were taken, the change in heating was made gradually, without permitting the temperature of the wire to change. Observation 1 was at room temperature. Observation 2 was with current heating. Without permitting more than a few degrees variation in temperature the current in the wire was decreased while that in the heater was increased. Observation 3 was with external heating. The temperature was then increased and observation 4 taken. Again the method of heating was gradually changed until observation 5 was secured with internal heating at practically the same temperature. In the same way 6 and 7; 8 and 9; 10 and 11 were taken. The results show in a striking manner that the changes accompanying current heating are only temperature effects. The tests of the tenth day with internal heating gave Series 8.

In any single series of this group the permanent changes with treatment do not appear prominent. But a comparison of the eight curves, Fig. 5, reveals a gradual increase of Young's modulus from day to day. This was caused undoubtedly by the continued application of the additional weight which caused a very small gradual stretching.

Effect of the Period of Rest.—Two days after the observations of Series 8 a measurement was taken at room temperature after which the wire was undisturbed for 106 days. This last observation appears with Series 9, Fig. 7, and a comparison with point 1 shows a slight recovery of the wire during the long rest. Nine other observations were then taken with an idea of determining whether or not the modulus would remain low upon heating. This proved to be the case both for external and current heating as is clearly brought out by comparison with the dotted line which is the Series 8 curve. Two days later, as shown by Series 10, further heating and testing brought the specimen back to its former state

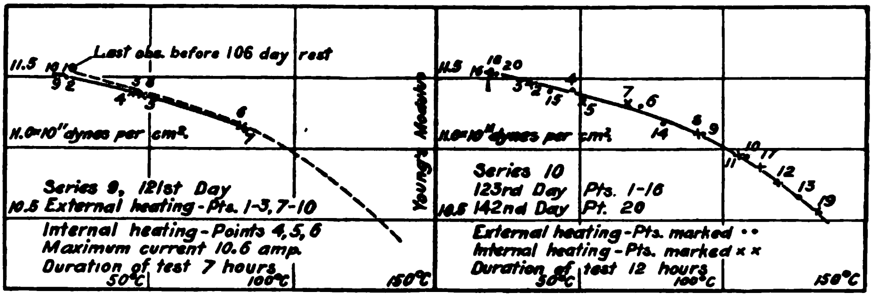

Fig. 7.

Results of tests upon specimen No. 3 after 106-day rest.

for low temperatures although at high temperatures greater values of Young's modulus were observed than ever before. Too much stress must not be laid upon these slight changes in the wire. The difference between Series 9 and Series 8 is small and may have its origin in a slight change in the working condition of the apparatus caused by its period of idleness. The important fact is that no great change occurred and the wire was in practically the same condition as when left. The explanation of the difference in slope in some of the curves is that the experimental error is of about the amount of the variation. The total change in Young's modulus over the entire temperature range is only 10 per cent. and the difference in stretch which this represents corresponds to less than one revolution of the micrometer head. In order to show this variation the scale to which Young's modulus is plotted has to be so large that the errors of observation become appreciable. When the magnitude of the probable error is taken into consideration the consistency of the curves taken under such a variety of conditions is remarkable.

Conclusions.

The following conclusions apply to the sample of copper wire that has been studied. I am of the opinion that other specimens of copper will yield results differing only in the magnitude of the changes, and believe that the results are very suggestive of the effects that can be expected in other metals. But work with iron wire now under way and certain results of other investigations to which reference is made later makes me feel that too great caution cannot be exercised in making general conclusions from observations upon particular samples.

From the preliminary observations and the tests upon specimens Nos. 2 and 3 we reach these conclusions:

1. A copper wire can be brought to a steady elastic state in which the stretch modulus becomes a function of temperature. In the present instance it was brought about by repeated stretching and heating and cooling over a range of temperature of 20° C. to 150° C. The preliminary tests show that the rate at which the heat was applied or at which the wire was cooled, the length of time the temperature was maintained, and the thermal route by which a given temperature was reached had no apparent effect upon the value of the modulus at any given temperature. These same facts are brought out still more convincingly by the extended work upon specimens 2 and 3, which also show that permanent changes in the modulus can be practically eliminated by a relatively small amount of heating and stretching, which if continued for a longer time renders them negligible.

2. Heating by an electric current has no effect other than that caused by the accompanying temperature. This was proved for one temperature by the results of Table I. and at a number of different temperatures by the work of Series 7, Wire 2, shown in Fig. 6, in which the heating was alternately by current and the external source.

Further proof with step by step heating is also furnished by the identical nature of the results recorded in the four curves of Fig. 4, two curves of which are for current and two for external heating. Conclusive evidence is afforded by the long series of experiments carried out upon the third specimen, in which every possible way of varying the methods of heating was attempted without detecting any difference in the results.

3. Young's modulus of a copper wire decreases with increase of temperature at an increasing rate. In the case of the specimen studied, the amount of decrease at different temperatures in terms of per cent. of the value of the modulus at 20° C. is as follows: 40° C., 0.6 per cent.; 60° C., 1.7 per cent.; 80° C., 2.9 per cent.; 100° C., 4.6 per cent.; 120° C., 7.0 per cent.; 140° C., 10.0 per cent. At 20° C. the modulus of the sample in the steady elastic state was 11.5×10^{11} dynes per cm^2.

The true nature of the temperature change was first shown by the work with specimen 2 as represented by the curves of Figs. 4 and was fully substantiated by the further work with specimen 3 which yielded identical results.

4. Heating and repeated stretching increases Young's modulus. As is shown by the results with specimen 3 there is an apparent increase of about 5 per cent. caused by the first four heatings and the accompanying stretching, which is thought to be due in part to the straightening out of the kinks. But there was a further increase of 2 per cent., which was a true history effect, although caused probably as much by the repeated stretching as by the heating.

Comparison with Results of Others.

As has already been stated previous results upon the effect of current do not agree. A comparison of these with the present work will not be attempted as the degree of accuracy in the latter is far greater. The conclusion that there is no effect of current upon copper other than that caused by temperature can be accepted to an accuracy of less than 1 per cent.

An interesting comparison regarding the history effect and the magnitude of change with temperature is furnished by the work of Shakespeare,[1]

[1] Loc. cit.

who used interference methods to determine the modulus at 13° C. and at 100° C. He does not compute the value of the modulus but gives the change from 13° C. to 100° C. as 3.6 per cent. For this range the present specimen shows a change of 5 per cent. Shakespeare also found that the modulus increased with continued heating and cooling, until a permanent state was reached. The first heating produced a sudden increase of several per cent. which was followed by a gradual change. Nine heatings produced a total increase of 12 per cent. The permanent change described in this paper was of the same kind and amounts to 7 per cent.

In the following comparison of results upon the temperature effect the bracketed figures are taken from our own curves. At 20° C. our value of Young's modulus was 11.5×10^{11} dynes per cm^2. Miss Noyes[1] found the modulus of a specimen of copper to be 12.02 at 20° C. This and another specimen tested at temperatures up to 150° C. gave a uniform decrease of the modulus which computed for 20° C. to 140° C. gives a change of 8.5 per cent. and 16 per cent. respectively [10 per cent.]. At 17.4° C. Gray, Blyth, and Dunlop[2] found the modulus of a sample of commercial copper to be 11.15 and of hard drawn electrolytic copper at 19.5° C. to be 12.9. They made tests over a range of 100° C. and reported a uniform rate of decrease which computed for 20° C. to 100° C. gives for the two samples changes of 1.2 per cent. and 3.4 per cent. respectively [4.6 per cent.].

Slotte[3] found for two specimens changes of 6.6 per cent. and 4.2 per cent. respectively [1.5 per cent.], for a temperature increase from 20° C. to 60° C. The moduli at 20° C. were respectively 12.4 and 12.7. The more important point is that he did not find a uniform rate of change. The modulus of the former specimen decreased at an increasing rate while the latter shows a decrease at a decreasing rate. Decrease of the modulus at an increasing rate is also indicated by the work of Wertheim.[4] If his results at 15° C., 100° C., and at 200° C. are plotted and a smooth curve drawn it is almost identical with our own curves, except that the values are about 10 per cent. lower. Regarding the nature of the change observations on the torsion modulus are valuable although too great stress must not be placed on them. Kohlrausch and Loomis[5] made observations upon copper at various temperatures. They found an increasing rate of change as the temperature increased. Computed for 20° C. to 100° C. the change is 4.2 per cent. [4.7 per cent.], and for 20° C. to 140° C. 7.5 per cent. [10 per cent.]. Slotte[6] has also made a study

[1] Loc. cit.

[2] Loc. cit.

[3] Loc. cit.

[4] Loc. cit.

[5] Loc. cit.

[6] Loc. cit.

of the torsion modulus of copper and finds the same increasing rate of change. Corresponding values from his work are 5.9 per cent. and 8.3 per cent.

The results that have been cited must be considered from two standpoints, first as to the general nature of the changes of Young's modulus, whether uniform or otherwise, and secondly, regarding the numerical values.

Examination of the methods of those who have reported a uniform decrease shows that their work was not of sufficient accuracy to have detected the variation from a linear relation found by others. We are not certain how much importance should be attached to the work of Slotte upon Young's modulus. He worked also with aluminum, iron, and platinum as well as copper and found a decreasing rate of change. None of these results seem to have been repeated. The torsion modulus can be determined to a much higher degree of accuracy and Slotte's recent work upon the torsion modulus of all these metals shows an increasing rate of change. Since the evidence that is available points toward a similarity in the nature of the temperature change of the two moduli this raises a question as to whether Slotte's former results upon Young's modulus are a true temperature effect.

With the results of Wertheim and of Slotte upon one specimen agreeing with our own and the work of Kohlrausch and Loomis and of Slotte upon the torsion modulus showing the same general type of change, I believe that the conclusion that Young's modulus of copper decreases with increase of temperature at an increasing rate has sufficient corroboration.

A comparison of the numerical values of Young's modulus and of the temperature coefficient, ample allowance being made for experimental error, leaves no doubt as to the importance of chemical purity, method of preparation, and size of specimen. It is possible that samples of copper may be found that will show effects peculiar to current heating, or will not give modulus-temperature curves of the simple form that I have found, but I am inclined to believe the main differences will be found in the magnitude of the coefficients. Undoubtedly further work will reveal some relation between the chemical composition, the coefficient of linear expansion, the electrical conductivity, and other physical constants, and the value of Young's modulus and its rate of change with temperature. Investigation is under way upon other metals in order to study the effect of current, to determine the temperature coefficient of Young's modulus, and to study the relation between the temperature changes of the two elastic moduli.

In conclusion I wish to acknowledge indebtedness to the staff of the physical laboratory of the State University of Iowa for their interest in the work and especially to Professor G. W. Stewart for suggesting the problem and to Professor J. N. Pearce, of the department of chemistry, for the chemical analysis.

Physical Laboratory
State University of Iowa,
August, 1913.

THE EFFECT OF SPACE CHARGE AND RESIDUAL GASES ON THERMIONIC CURRENTS IN HIGH VACUUM.

BY IRVING LANGMUIR.

WHEN a carbon or metal filament is heated in a vacuum and surrounded by a positively charged metal cylinder, it is well known that electrons are given off by the hot solid. This effect in lamps has been commonly known as the Edison effect and has been rather fully described in the case of carbon lamps by Fleming.[1]

Richardson and others have studied quantitatively the ionization produced by hot solids, especially from heated platinum, and have collected a large amount of data. It has generally been found that the saturation current is independent of the pressure of the gas and increases rapidly with increasing temperature of the filament. However, certain gases were found to have very marked effects; for example, traces of hydrogen were found to enormously increase the saturation current obtained from hot platinum.[2] Recent investigations have shown[3] that at least in some cases the current is due to secondary chemical effects.

Pring and Parker[4] showed that the current obtained from incandescent carbon could be cut down to very small values by progressive purification of the carbon and improvement of the vacuum. They conclude that "the large currents hitherto obtained with heated carbon cannot be ascribed to the emission of electrons from carbon itself, but that they are probably due to some reaction at high temperatures between the carbon, or contained impurities, and the surrounding gases, which involves the emission of electrons." Pring and Parker observed also that the ionization (or rather thermionic current) "increased only very slightly with the temperature above 1800°."

The effect of these publications, together with that of Soddy,[5] who noticed similar effects with a Wehnelt cathode, has been to cast doubt on the existence of a thermionic current in a perfect vacuum and from pure metals. The opinion seems to be gaining ground, especially in Germany, that the emission of electrons from incandescent solids is a secondary effect produced by chemical reactions, or at least is caused by the presence of gas.

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[1] Phil. Mag., *42*, p. 52 (1896).

[2] H. A. Wilson, Phil. Trans., *202*, 243 (1903).

[3] Fredenhagen, Ver. d. phys. Ges., *14*, 384 (1912).

[4] Phil. Mag., *23*, 192 (1912).

[5] Nature, *77*, 53 (1907).

With the above-mentioned exceptions, it has generally been found that the thermionic current increased with the temperature at a very high rate. The relation between current and temperature was usually accurately represented by Richardson's equation

$$i = a\sqrt{T}e^{-\frac{b}{T}}, \tag{1}$$

where a and b are constants and i is the saturation current at the absolute temperature T.

If the older values of a and b as found, for example, for carbon, are substituted in the above equation and the currents for very high temperatures (above 2500°) are calculated, values of many amperes or even thousands of amperes per square cm. are usually obtained. This raises the question why in ordinary incandescent lamps very large thermionic currents do not occur.

There is every reason to think that the thermionic current from tungsten should be fairly large. When we run a tungsten lamp up to 2 or even 2.5 times its normal voltage (filament temperature 2900–3400° K.) we should therefore expect to get thermionic currents of several amperes between the two ends of the filament. Simple observation of a lamp run under such conditions indicates that this is not the case. For example, consider a lamp which takes 110 volts and 0.3 ampere when running at normal specific consumption (1.25 watts per candle). By raising the voltage to 250, the temperature of the filament will be brought to about 3000° K. and the current is then about 0.45 ampere. The resistance of the filament has thus increased from 366 ohms up to 555. The total surface of the filament is nearly half a square cm., yet it is evident that if there is any thermionic current between the two ends of the filament, it cannot exceed a few hundredths of an ampere. This apparent discrepancy between the results of calculation by Richardson's equation and the facts observed with a tungsten lamp seemed at first to confirm the growing opinion that in a very high vacuum the thermionic current is very small, if not entirely absent.

Experiments on the Edision effect in tungsten lamps, made some time ago by the writer, throw a great deal of light on the cause of the apparent failure of Richardson's equation at high temperatures. The observations therefore seem of sufficient interest to warrant their publication.

EXPERIMENTS ON EDISON EFFECT IN TUNGSTEN LAMPS.

Some lamps were made containing two single loop (hairpin) tungsten filaments with separate leading-in wires. Each loop could thus be run separately. The lamps were given a specially good lamp exhaust, which involved heating them to 360° for an hour while being exhausted with a mercury pump. A trap immersed in liquid air was placed between the pump and the lamp to condense out water vapor, carbon dioxide and mercury vapor. The filaments were then connected in series and the lamps run at a specific consumption of about 1 watt per candle for fifteen minutes, to drive the gas from the filaments. The lamps were then sealed off from the pump and the filaments were again heated, this time being run at 0.4 watt per candle for a few minutes, to age the filaments and improve the vaccuum (clean-up effect).

Experiments were then undertaken to measure the thermionic currents that flowed across the space between the two filaments when one was heated to various temperatures while the other was connected to a constant source of positive potential of about 125 volts. A milliammeter was connected in series with the cold filament.

When the temperature of the cathode filament was raised to about 2000° K. a current of about 0.0001 ampere was observed to flow between the two filaments. As this temperature was raised the thermionic current rose very rapidly, until at about 2200° K. it was about .0006 ampere. As the temperature was raised above 2200° K., *no further increase in the thermionic current occurred*, even when the filament was heated nearly to the melting-point (3540° K.). By raising the voltage on the anode to about 250 volts, the thermionic current increased to about .0015 ampere. It required, however, a temperature about 200° higher to reach this current than had been found necessary to reach the maximum current at the lower voltage. At temperatures below 2200° K., the current was practically the same with 125 as with 250 volts.

The results of a later and more accurate experiment are given in Fig. 1. The filament used for these measurements consisted of a single loop of drawn tungsten wire, of diameter .0069 cm. and total length of 10.84 cm. and area of 0.234 sq. cm. A similar filament, at a distance of about 1.2 cm., served as anode. Both filaments had been aged a couple of hours at high temperature and the vacuum thus obtained was certainly better than 10^{-6} mm.[1]

The temperatures of the filament were determined from the relation

$$T = \frac{11,230}{7.029 - \log_{10} H},$$

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[1] Judging from measurements on similar lamps made by means of the "molecular" gage described by the writer, PHYS. REV., 1 (2), 337 (1913).

where H is the intrinsic brilliancy of the filament in international candles per sq. cm. of projected area.[1]

The points indicated by small circles (Fig. 1) are experimentally determined. Two different anode voltages were used: 240 and 120 volts, with respect to the negative terminal of the filament which served as hot cathode. The voltage used to heat the cathode varied from about 7 to 15 volts, so the *average* potential difference between anode and cathode was somewhat less than 240 and 120 volts. The curve given for 60 volts was determined from other experiments devised especially to determine the effect of voltage variations.

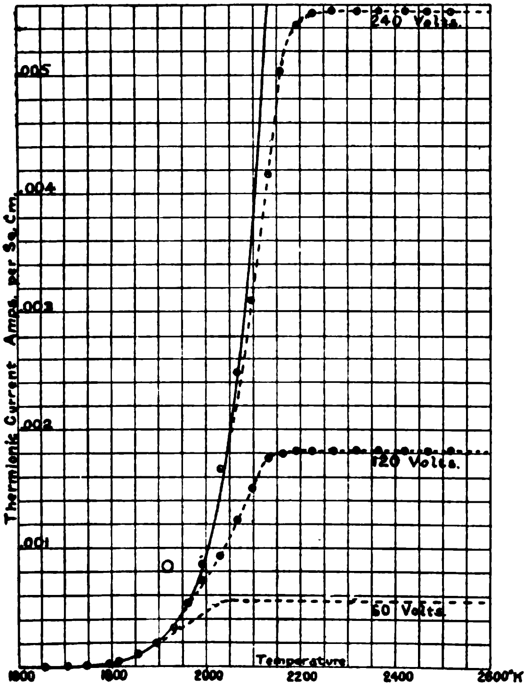

Fig. 1.

It is seen from these curves that at low temperatures the current for all three voltages is the same, but that as the temperature is raised the currents at the lower voltages fall below those for higher voltages and finally each in turn reaches a constant value.

By plotting (log. $i - \frac{1}{2}\log T$) against $1/T$ it was found that all the points on the 240-volt curve up to a temperature of about 2150° lay very close to a straight line. This indicates that these results can be expressed by Richardson's equation. From the slope and position of the line, the values of a and b of Richardson's equation were found to be

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[1] The derivation of this formula will soon be published, probably in the PHYSICAL REVIEW.

$$a = 27 \times 10^6 \text{ (amperes per sq. cm.)},$$
$$b = 55{,}600 \quad \text{(degrees)}.$$

The heavy black curve of Fig. 1 was calculated by plotting Richardson's equation, using these values of a and b. The agreement between this curve and the experiments at low temperature is nearly perfect; in fact, much better than can be seen from Fig. 1.

It is seen that each experimentally determined curve can be divided into three parts:

1. A part which follows Richardson's equation accurately.
2. A part which consists of a horizontal straight line; that is, a part in which the current is independent of the temperature of the filament.
3. A transition curve between these.

The horizontal part of the curve was of particular interest. The current being independent of the temperature of the filament is probably independent of the nature of the cathode. It seemed possible, however, that it might be dependent on the anode. Several experiments were undertaken to determine the factors which governed the value of this new kind of "temperature" saturation current. It was found that it was very largely affected by any one of the four factors:

1. Voltage of anode.
2. Presence of magnetic field.
3. Area of anode.
4. Distance from anode to cathode.

It is especially noteworthy that none of these factors had any influence on the thermionic current over the first part of the curve; *i. e.*, that part which follows Richardson's equation. That is, the constants a and b were not affected by voltage, or magnetic field or distance or area of anode.

After trying out several hypotheses which suggested themselves, it finally occurred to the writer that this temperature saturation might be due to a space charge produced by the electrons between the cathode and anode. The theory of electronic conduction in a space devoid of all positive charges or gas molecules seems to have been strangely neglected. It has apparently always been taken for granted that positive ions are present, or at least a sufficient amount of gas, so that the motion of the electrons follows the laws of diffusion. J. J. Thomson[1] gives the differential equations that apply to the calculation of electron conduction through space, and suggests that a method for the determination of *e/m* could be worked out in this way. He apparently does not fully integrate the equations or realize their application to ordinary thermionic currents.

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[1] Conduction of Electricity through Gases, 2d edition, p. 223.

THEORY OF ELECTRONIC CONDUCTION IN A SPACE DEVOID OF MOLECULES OR POSITIVE IONS.

In order to form a clear conception of the problem before us, let us consider (see Fig. 2) two infinite parallel planes, *A* and *B*, one of which, *A*, has the properties of an incandescent solid; that is, we assume that it emits low velocity electrons spontaneously. The other, plane *B*, we consider to be positively charged.

Now if the temperature of the plate *A* is so low that few or no electrons are emitted, then the potential between the two plates will vary linearly between the two, as indicated by the line *PT*.

As the temperature of *A* is raised, electrons are emitted. Under the influence of the field these pass across the space from *A* to *B* and thus constitute a current of magnitude *i* (per sq. cm.).

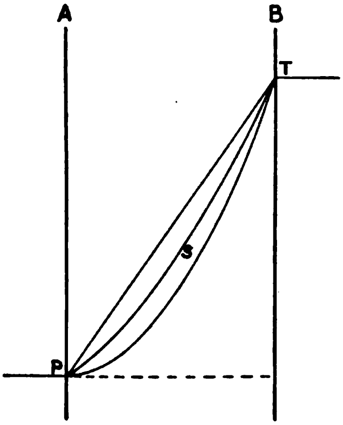

Fig. 2.

These electrons move with a velocity which depends on the potential drop through which they have passed. Let us assume, as a first rough approximation, that they move with constant velocity across the space. Then there will be in the unit volume a space charge ρ equal to i/v, where v is the velocity of the electrons. If the velocities are uniform, the space charge will be uniform and it follows from Laplace's equation

$$\Delta V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -4\pi\rho \tag{2}$$

that

$$\frac{d^2 V}{dx^2} = -4\pi\rho. \tag{3}$$

If we consider ρ constant and negative (for electrons), we see from this equation that the potential distribution between the two plates takes the form of a parabola, as indicated by the curve *PST*.

If the temperature of the plate *A* be increased still further, the electron current increases so that the potential curve finally becomes a parabola with a horizontal tangent at *P*.

If we assume that the electrons are given off from the plate A with practically no initial velocity, we see that the current cannot increase beyond the point where the potential curve becomes horizontal at P, for any further increase of current would make the potential curve at P slope downwards and the electrons would be unable to move against this unfavorable potential gradient.

In other words, we see that the effect of the space charge is to limit the current. A further increase in the temperature of the plate A would then not cause an increase of current.

Electron Current between Parallel Planes.—Let us now attempt a more rigorous solution of the problem.

It has been shown by Richardson and others that the mean kinetic energy of the thermions is closely equal to that of gas molecules at the same temperature. This indicates that they have velocities so low that very few of them are capable of moving against a negative potential of more than a couple of volts. Since the voltages applied to the anode are much larger than this, we may assume, for convenience, that the electrons are given off by the plate A without initial velocity.

Now let V be the potential at a distance x from the plate A. The kinetic energy of an electron when it has traveled the distance x from the plate will thus be

$$\tfrac{1}{2}mv^2 = Ve. \tag{4}$$

The current (per unit area) carried by the electrons at any place will be

$$i = \rho v. \tag{5}$$

For convenience, we take e and ρ positive even for electrons. Equation (3) thus becomes (in electrostatic units)

$$\frac{d^2V}{dx^2} = 4\pi\rho. \tag{6}$$

These three equations enable us to express V as a function of x and i. By eliminating ρ and v from (4), (5) and (6), we obtain

$$\frac{d^2V}{dx^2} = 2\pi\sqrt{2}\sqrt{\frac{m}{e}}\frac{i}{\sqrt{V}}. \tag{7}$$

Multiply this by $2\cdot dV/dx$ and integrate

$$\left(\frac{dV}{dx}\right)^2 - \left(\frac{dV}{dx}\right)_0^2 = 8\pi i\sqrt{\frac{2mV}{e}}. \tag{8}$$

Now if there is an opposing (negative) potential gradient at the surface of the plate A, *no current* will flow. If there is a positive potential gradient all the electrons that are given off from the plate A will reach B, so that the current that flows will be determined by Richardson's equation. The case that we are interested in is that in which the current is less than the saturation current and is determined by the voltage of the anode. Evidently for this case the potential gradient at the plate A is zero; that is,

$$\left(\frac{dV}{dx}\right)_0 = 0,$$

whence from (8) by extracting the square root:

$$\frac{dV}{dx} = \sqrt{8\pi i}\sqrt[4]{\frac{2mV}{e}}. \tag{9}$$

Integrating and solving for i, we obtain:

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{x^2}. \tag{10}$$

This equation[1] gives the maximum electron current density between two infinite parallel plates with the distance x between them and with a potential difference V. This equation holds only where the initial velocity of the electrons at the plate A is negligible compared to that produced by the potential V. It does not hold at such high voltages that the electrons move with velocities approaching that of light.

Taking $e/m = 1.77 \times 10^7$ E.M. units, reducing to E.S. units and substituting in (10) and then reducing to volt, ampere units, we obtain from equation (10):

$$i = 2.33 \times 10^{-6}\frac{V^{\frac{3}{2}}}{x^2}, \tag{11}$$

where i is the maximum current density in amperes per sq. cm., x is the distance between the plates in centimeters, and V is the potential difference in volts.

Electron Current between Concentric Cylinders.—Let us consider a wire of radius a placed in the axis of a cylinder of radius r. Let i be the thermionic current per unit of length from the wire.

For the case of symmetrical cylindrical coördinates, Laplace's equation becomes[2]

$$\Delta V = \frac{1}{r}\frac{d}{dr}\left(r\frac{dV}{dr}\right) = 4\pi\rho$$

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[1] Since submitting this paper for publication the attention of the writer has been called to the fact that C. D. Child (Phys. Rev., *32*, 492, 1911), has already derived this equation. He has, however, applied it only to the case where the conduction takes place solely by positive ions.

[2] Weber's Differential Gleichungen, 1900, Vol. 1, p. 98.

or

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right) = 4\pi\rho r. \tag{12}$$

The equation corresponding to (5) is

$$i = 2\pi r\rho v. \tag{13}$$

These two equations, together with equation (4), which also applies to this case, give us

$$r\frac{d^2V}{dr^2} + \frac{dV}{dr} = i\sqrt{\frac{2m}{eV}}. \tag{14}$$

This equation probably cannot be directly integrated, but it is possible to obtain a result in terms of a series. The final solution takes the form

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{r\beta^2}, \tag{15}$$

where β is a quantity which varies from 0 to 1. The value of β can be obtained by substituting equation (15) in (14) and placing

$$r = ae^{\gamma}. \tag{16}$$

Equation (14) is thus reduced to

$$3\beta\frac{d^2\beta}{d\gamma^2} + \left(\frac{d\beta}{d\gamma}\right)^2 + 4\beta\frac{d\beta}{d\gamma} + \beta^2 - 1 = 0. \tag{17}$$

The solution of this equation gives

$$\beta = \gamma - \tfrac{2}{3}\gamma^2 + \tfrac{11}{120}\gamma^3 - \tfrac{47}{3300}\gamma^4 + \cdots, \tag{18}$$

where

$$\gamma = ln\frac{r}{a}.$$

Mr. E. Q. Adams, of this laboratory, has calculated the values of β for various values of r/a and has shown that the value of β rapidly approaches unity and that for all values of r/a greater than 10, β may for most purposes be taken equal to unity. The following table was prepared from Mr. Adams' data:

Table I.

r/a	β^2	r/a	β^2
1.00	0.000	5.0	0.755
1.25	0.045	6.0	0.818
1.50	0.116	7.0	0.867
1.75	0.200	8.0	0.902
2.00	0.275	9.0	0.925
2.50	0.405	10.0	0.940
3.00	0.512	15.0	0.978
4.00	0.665	∞	1.000

Since in practical cases the diameter of the cylinder around the wire is usually much more than ten times that of the wire, the formula (1) may usually be written

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\,\frac{V^{3/2}}{r}. \tag{19}$$

That is, the maximum electron current from a small wire is independent of the diameter of the wire, inversely proportional to the radius of the enclosing cylinder and proportional to $V^{3/2}$.

Substituting numerical values for e/m and reducing to ordinary electrical units (volts, amperes, cm.) equation (19) becomes

$$i = 14.65 \times 10^{-6}\,\frac{V^{3/2}}{r}. \tag{20}$$

Electron Current between Electrodes of Other Shapes.—It can be shown that between electrodes of any shape the maximum electron current varies with $V^{3/2}$. Let us consider a system in which we have the maximum electron current with the potential difference V. Then Laplace's equation

$$\Delta V = 4\pi\rho \tag{2}$$

holds for such a space, as well as the two equations

$$i = \rho v \tag{5}$$

and

$$\tfrac{1}{2}mv^2 = Ve. \tag{4}$$

Now let us increase the voltage in the ratio $1 : n$ and increase the current in the ratio $1 : n^{3/2}$. Equations (5) and (4) thus become

$$n^{3/2} i = \rho v,$$

$$\tfrac{1}{2}mv^2 = nVe.$$

Eliminating v from these, and solving for ρ, we get

$$\rho = ni\sqrt{\frac{m}{2Ve}}.$$

From this we see that ρ has been increased n fold. However, since V has been increased also n fold, Laplace's equation (2) still holds. Hence we see that increasing the current by a factor $n^{3/2}$ and increasing the voltage by the factor n, leads to a condition which still satisfies the three equations (2), (4), and (5). This is, however, equivalent to increasing the current proportionally to $V^{3/2}$. We thus see that whatever the configuration of the electrodes, the *maximum* electron current varies with $V^{3/2}$.

DISCUSSION OF THE THEORY.

The foregoing theoretical considerations have indicated that in a space devoid of positive ions, or gas molecules, the space charge caused by the electrons limits the current that flows between a hot cathode and cold anode under a given difference of potential. It now remains to compare the maximum currents obtained in the experiments, with those calculated from the equations that have been derived.

Let us consider the data given in Fig. 1. The maximum electron current at 120 volts was .000426 ampere from the hot filament, or .00182 ampere per sq. cm. At 240 volts the total current was .00130 ampere, or .00556 ampere per sq. cm. Since we are not dealing with parallel plane electrodes, nor with concentric cylinders, neither equation (11) nor (20) will apply rigorously. We are, however, mainly concerned in determining whether the space charge is an adequate explanation of the observed limitation of the thermionic current, and therefore can test out the two equations by calculating the distances which would have to exist between plane or cylindrical electrodes in order to give the observed thermionic currents.

We will first test out equation (11), which should apply to parallel plane electrodes. Let us take the observed values of V and i and calculate x. We thus obtain:

For $V = 120$ volts and $i = .00182$, we find $x = 1.30$ cm.;

$V = 240$ volts $i = .00556$, we find $x = 1.25$ cm.

Our formula thus indicates that the current density between parallel plane electrodes about 1.3 cm. apart would be the same as that observed. This is, however, very close to the actual distance between the electrodes. The very close agreement is probably due to the counter-balancing of two factors: first, the weakening of the electrostatic field, due to the flare of the lines of force around the wires, and second, the reduction of the intensity of the space charge owing to this same flare.

Let us now test the equation (20), which should apply to concentric cylinders. Since the wire was 10.8 cm. long, the values of i (amperes per cm.) were .0000394 at 120 volts and .000120 at 240 volts. Substituting these values in (20) and solving for r we obtain

at 120 volts $r = 490.$ cm.,

240 volts $r = 450.$ cm.

We see that the radius of a cylindrical anode would have to be very large (470 cm.), in order to give only the observed thermionic current. This result, however, appears perfectly reasonable, for the field produced by a small wire anode is naturally much weaker than that produced by a cylindrical anode surrounding the cathode.

The numerical values obtained from these equations are certainly of the right order of magnitude and agree as well with the experimental results as could be expected when the shape of the electrodes departs so far from those assumed in the calculations.

We have seen that the theory leads us to the conclusion that for electrodes of any shape the maximum thermionic current should vary with $V^{\frac{3}{2}}$. This can be readily tested out from the experiment. The ratio of the currents at the two voltages is 3.05. Taking the 2/3 power of this ratio, the voltage ratio should be 2.10, whereas actually it was 2.0. However, it must be remembered that the voltage of the anode was measured from the negative end of the filament, so that the average voltage drop from anode to cathode was about seven or eight volts less than those given. This would give for the voltage ratio 232 : 112, or 2.07, as against the 2.10 calculated by the three-halves power law.

Several experiments have been undertaken to study the relation of maximum current to voltage over a wide range of voltage. Voltages from 10 volts up to 800 volts have been tried and the results plotted on logarithmic paper. From the slopes of the resulting lines the exponent of the voltage was calculated. Values varying from 1.5 to 1.7 have been obtained. Under certain conditions, to be described in more detail later, values much higher than these are sometimes obtained.

The above considerations indicate that the space charge produced by the electrons is a sufficient cause for the limitation of current observed in the experiments.

Effect of Residual Gases on Constants of Richardson's Equation.

In some of the early experiments on the thermionic current between two tungsten filaments, extremely variable results were obtained for the constants of Richardson's equation. In many cases, however, when anode potentials as high as 150 or 250 volts were applied, a blue glow appeared in the lamp, indicating ionization of the residual gas. To get rid of this, the two filaments were connected in series and both heated to a very high temperature (2900° K.) for a few minutes. This "cleans up" the vacuum to an extremely high degree. The writer is publishing a series of articles in the Journal of the American Chemical Society on the clean up of various gases in a tungsten lamp. It has been found that with a very high temperature of the filament, all gases except the inert ones may be removed practically quantitatively. This treatment of the lamp to improve the vacuum resulted in a marked change in the constants of Richardson's equation and also changed the maximum thermionic currents.

To still further improve the vacuum in some cases, the entire bulb was immersed in liquid air and the filaments were again heated to high temperature for a short time. This sometimes resulted in a further change in the thermionic current.

These effects were clearly due to traces of residual gas. To study them in more detail, some experiments were carried out in which lamp bulbs containing two filaments (or sometimes three) were connected to a vacuum system consisting of Töpler pump, sensitive McLeod gage and trap immersed in liquid air, placed directly below the lamp. The lamps were exhausted to less than .0001 mm. and heated for one hour to 360° C., to drive water vapor and carbon dioxide into the liquid air trap. No stop-cocks were used in the entire system, so that vapors of vaseline, etc., were avoided. The liquid air trap prevented the entrance of mercury vapor into the lamp. Care was taken to keep liquid air on the trap day and night during the whole experiment.

The lamp bulb was about 3.5 cm. diameter and was connected to the rest of the vacuum system by a tube attached at the top of the bulb and bent into a goose neck. In this way the bulb could be immersed completely in liquid air if desired.

After exhaustion of the bulb and ageing of the filament at high temperature, a run was made with 177 volts on the anode, but without liquid air on the bulb. The pressure, according to the McLeod gage, was .00012 mm.

The constants of Richardson's equation were found to be

$$a = 22.10^6 \text{ amps. per sq. cm.},$$

$$b = 55{,}800 \text{ degrees.}$$

Liquid air was now placed around the lamp bulb, and the thermionic current again determined. During this run the pressure was constant at .00007 mm.

The constants were then found to be:

$$a = 34 \times 10^6,$$

$$b = 55{,}500.$$

A plot of the curve, calculated from these data by Richardson's equation, is given in Curve I., Fig. 3, together with the experimentally determined points (Curve III.).

The effect of cooling the bulb in liquid air was thus to increase the thermionic current considerably (about 60 per cent. at 2000° K.). The filament was now run at 2130° K., at which temperature a thermionic current of .00214 amp. was observed. The liquid air was then removed from the bulb. The thermionic current fell rapidly to .00049 and then rose to .00184, at which it remained steady.

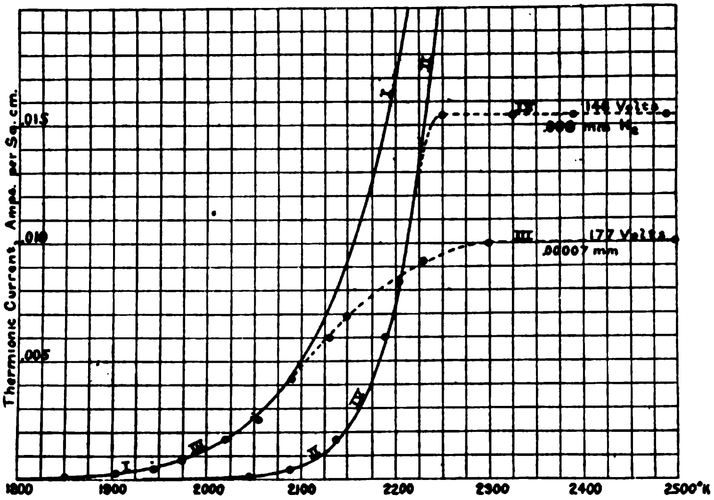

Fig. 3.

Hydrogen.—Pure hydrogen to a pressure of .012 mm. was now admitted. The thermionic current was rather variable, changing gradually with the time, but by running the temperature up and down several times, fairly consistent results were obtained. The average values of Richardson's constants were

$$a = 5.4 \times 10^{11},$$

$$b = 82{,}500.$$

The hydrogen had gradually cleaned up during these runs from 0.012 mm. to .006 mm.[1] The remainder of the hydrogen was now pumped out (down to .00011 mm.) and another run was made to determine the thermionic current in good vacuum. The results were

$$a = 4.3 \times 10^{12},$$

$$b = 85{,}000.$$

The pressure rose during this run from .00011 to .00052 mm.

The removal of the hydrogen thus produced relatively little effect, and certainly did not tend to cause *a* and *b* to return to the original values in a good vacuum.

[1] See paper on Active Modification of Hydrogen, Langmuir, J. Amer. Chem. Soc., *34*, 1310 (1912).

More hydrogen (.007 mm.) was now let in, and the constants were found to be

$$a = 7.6 \times 10^{18},$$

$$b = 115{,}000.$$

During this run the hydrogen cleaned up from .007 to .004 mm.

A plot of the curve calculated from Richardson's equation is given in Fig. 3 (Curve II.), together with the experimentally determined points (Curve IV.).

The general effect of the hydrogen had apparently been to permanently lower[1] the thermionic current, especially at low temperature. It had at the same time increased the value of the constant b to more than double its original value.

Effect of Bulb Temperature.—At this stage in the experiments it was found that touching the bulb with the fingers had a marked effect on the thermionic current. This was due to a temperature effect. With the filament at 2190° K. the current was .0011 amp. Warming the bulb slightly lowered the current to .0003. Placing ice water around the bulb raised the current to .0038. Liquid air, however, gave the same result as ice water. A run with the bulb in liquid air, with a pressure of .00025 mm. of hydrogen in the bulb, gave

$$a = 20.4 \times 10^{6},$$

$$b = 55{,}600.$$

These values are very close to those previously obtained with liquid air before any hydrogen had been let into the bulb.

Immediately after this run a beaker containing water at 62° C. was placed around the bulb. The pressure rose to .0017 mm. and the values of a and b became

$$a = 7.7 \times 10^{16},$$

$$b = 105{,}000.$$

A large number of runs were now made at different bulb temperatures. The results were similar to those already given, except that gradually the effect of heating the bulb became less marked and after a couple of days practically the same results were obtained with the bulb at 50° as at 0°. For example, two consecutive runs gave

$$\text{at } 0^\circ \quad a = 54.10^{6}, \quad b = 58{,}500;$$

$$\text{at } 53^\circ \quad a = 60.10^{6}, \quad b = 58{,}500.$$

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[1] The increase in the value of b in Richardson's equation much more than offsets the increase in a, so that at temperatures in the neighborhood of 2000°, the currents in hydrogen are very much smaller than the original currents in vacuum.

Before this condition of insensitiveness to bulb temperature had been reached, tests were made to see if the changes in the thermionic current were due to vacuum changes or absorption of gas by the filament. The effect of interchanging the two filaments was tried many times. That is, the filament which had previously been used as anode was made cathode and vice versa. In no case did this change make any material difference in the magnitude of the thermionic current. The heating of the bulb produced exactly the same effect, regardless of the previous history of the filament. The changes that did occur could clearly all be ascribed to vacuum changes caused by the absorption or evolution of gas by the bulb.

Water Vapor.—The fact that the temperature of the bulb was in some cases so much more important than the pressure of hydrogen indicated that it was the presence of water vapor that caused the decrease in the thermionic current and the increase in b. To test this out, the liquid air was removed for a couple of minutes from the liquid air trap below the lamp and then replaced. The effect of thus allowing water vapor to enter the lamp was to make the thermionic current extremely sensitive to the temperature of the bulb. This sensitiveness could be destroyed again by heating the bulb to 360° and cooling.

The conclusion to be drawn from these facts is that the decrease in the thermionic current is due to the presence of traces of water vapor. The McLeod gage gives no indication of such small amounts of water vapor, but the fact that little or no hydrogen is evolved by the action of the filament on the water vapor, together with the fact that the water vapor can remain days in the lamp before diffusing down into the liquid air trap, indicate that the pressure must be extremely low—probably not over 10^{-6} mm. Yet the evidence is strong that such pressures of water vapor have an enormous effect on the saturation thermionic current from tungsten.

Oxygen.—It had been known that water vapor in contact with a hot tungsten filament oxidizes the filament with the liberation of atomic hydrogen. It was therefore of interest to know whether the marked effect produced on the thermionic current by water vapor is due to this particular reaction or whether the same effect will not be produced by dry oxygen.

To test this out, the system was exhausted to a pressure of .00012 mm. The mercury in the Töpler pump bulb was raised so as to seal off the bulb and pure dry oxygen was admitted to the bulb. The quantity was chosen so that it would give a pressure of .005 mm. when allowed to flow out into the whole system by lowering the mercury in the pump bulb.

The filament (*A*) was now run at 2190° K., and the other filament (*B*) was charged 250 volts positively with respect to the cathode. The thermionic current was .0031 amp.

On lowering the mercury in the pump bulb and allowing the oxygen to enter the lamp bulb, the thermionic current dropped immediately to .00013; that is, to 4 per cent. of its original value. As the oxygen gradually disappeared, the current steadily rose in value, as follows:

	Pressure, Mm.	Thermionic Current.
On admitting oxygen	.005	.00013
After 5 minutes	.0003	.00030
After 10 minutes	.00016	.00090
After 15 minutes	.00014	.00164
After 20 minutes	.00010	.00230
After 28 minutes	.00007	.00270

After letting in another supply of oxygen, the thermionic current was determined at various temperatures and gave

$$a = 6.8 \times 10^{13},$$

$$b = 94{,}300.$$

The effect of oxygen is thus found to be quite similar to that of water vapor.

Nitrogen.—Experiments with nitrogen showed that this gas also usually decreased the thermionic current, although not so strongly as oxygen. Since nitrogen does not clean up as rapidly as oxygen, this gas was chosen for a series of experiments to determine whether other factors, such as anode voltage, had an influence on the Richardson constants in the presence of gas.

Effect of Anode Potential.—In one experiment a pressure of about .001 to .002 mm. of nitrogen was present in the bulb. A run was made with a potential of 220 volts on the anode, then a run with 100 volts, and then another run at 220 volts. The thermionic currents (milliamperes per sq. cm.) in the three runs were as follows:

TABLE II.

Temp.	220 Volts.	100 Volts.	220 Volts.
2045	....	0.34	0.29
2090	....	0.70	0.63
2140	....	1.54	1.29
2190	2.7	4.0	2.9
2250	6.3	4.9	7.0
2325	16.2	5.0	19.3
2390	21.0	5.0	20.0
Pressure of N_2 =	.0015 mm.	.0012 mm.	.0012 mm.

These results show that under certain conditions (low temperature and proper pressure of nitrogen) less current is obtained with 220 volts than with 100 volts. In this connection it may be said that these thermionic currents were reproducible and accurately measurable. The values changed gradually, however, as the nitrogen cleaned up.[1]

The following are typical runs (Table III.) selected from many that were made while the nitrogen was gradually disappearing:

TABLE III.

Temp.	Pressure .00067 Mm.		Pressure .00011 Mm.	
	100 Volts.	220 Volts.	100 Volts.	220 Volts.
2045	0.53	0.36	1.58	1.50
2090	1.02	0.86	2.9	2.90
2140	2.50	1.90	3.8	6.2
2190	4.2	4.50	4.4	9.8
2250	4.6	11.8	4.6	11.4
2325	4.8	13.8	....	11.8
2390	....	13.9	....	12.1

Thus, as the nitrogen cleans up, the thermionic current increases and tends to return to its original value. At the same time the peculiar effect of the anode voltage in causing less current to flow at high voltage also practically disappears.

All the experiments with nitrogen were made with the bulb surrounded with ice. This precaution, however, did not seem necessary in these runs, for at various times the ice was removed, but the thermionic current remained unchanged.

In order to investigate in more detail the effect of the anode potential at various pressures of nitrogen and different filament temperatures, a special experiment was undertaken. A lamp containing two single loop filaments in a large bulb was sealed to the same vacuum system and exhausted as before. The filaments were of .0124 cm. diameter and each 8.9 cm. long.

After ageing the filament, the thermionic current was measured at 120 and 230 volts; the constants a and b were:

$$\text{at } 120 \text{ volts} \quad a = 1.2 \times 10^{13}, \quad b = 83{,}000;$$

$$230 \quad `` \quad a = 4.7 \times 10^{12}, \quad b = 80{,}500.$$

On the average, even with currents so low that the space charge should have no effect, the thermionic current was about 20 per cent. less with

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[1] This is the electrochemical clean-up of nitrogen referred to by the writer in a paper on "The Clean-up of Nitrogen in Tungsten Lamps," Jour. Amer. Chem. Soc., *35*, 931 (1913).

120 than with 230 volts. This effect, which is just the opposite of that noted in the preceding experiment, is of fairly common occurrence when very special precautions are not taken to avoid traces of certain gases.

The effect of oxygen on the thermionic current with different anode potentials was next tried. In every case the current was greatly reduced by the presence of this gas. The currents obtained with 120 volts and with 230 volts were always practically identical.

Another measurement of the thermionic current in good vacuum (.0001 mm.) at 120 and 240 volts gave

$$a = 1.1 \times 10^{11},$$

$$b = 74{,}000.$$

The curve obtained by Richardson's equation with these constants is given in Curve I., Fig. 4, while Curves II. and III. are drawn through the experimentally determined points.

A pressure of 0.0021 mm. of nitrogen was now introduced and the following measurements made at 120 and 235 volts. The results are expressed in milliamperes per sq. cm.

Table IV.

Filament Temp.	Pressure .0021 Mm. Nitrogen.	
	Anode 120 Volts.	Anode 235 Volts.
2000	.132	.130
2050	.278	.283
2100	.515	.552
2150	1.07	1.42
2200	2.90	3.90
2250	6.4	8.0
2300	12.9	16.6
2350	>26	>26
$a =$	1.66×10^9	2.2×10^{10}
$b =$	68200	73200

These results are plotted (Curves IV., V., Fig. 4) for comparison with the preceding run in a vacuum. It is to be noted that at temperatures up to 2050° the thermionic current, even with such a high pressure of gas, is not as much affected by the anode voltage as it had previously been found to be in a "good" vacuum. The presence of the nitrogen has, however, entirely removed all limitation of the current by space charge at the higher filament temperatures.

Some runs were now made with the filament at fixed temperatures while the anode voltage was varied over a wide range. In most cases the pressure of nitrogen was kept as nearly constant as possible at .0025 mm.; in some runs, however, the effects produced by a pressure of .0010 mm. were studied.

The data from three runs with the filament at 2100° are given in Fig. 5. The points along Curves I. and II. were obtained with .0025 and .0010 mm. pressure of nitrogen. The nitrogen was then pumped out to a pressure of .00016 mm., and the points along Curve III. were then obtained.

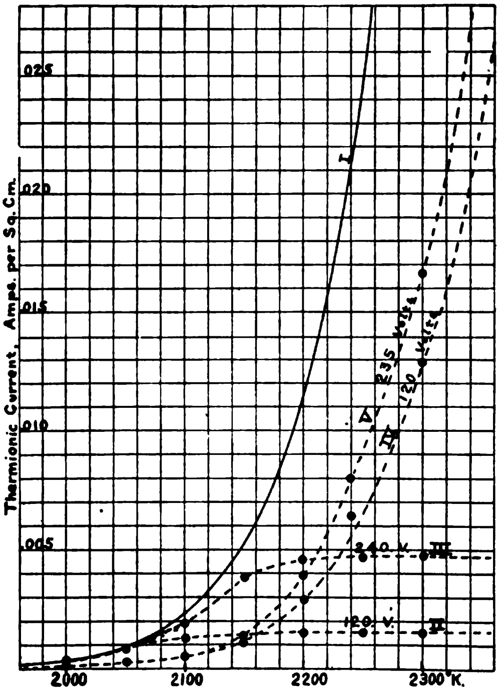

Fig. 4.

These curves help clear up several points that had been left very indefinite by the previous data. At anode potentials below 80 or 90 volts the effect of nitrogen is evidently to increase the thermionic current materially. But above a certain critical potential, which is higher the lower the pressure of nitrogen, the thermionic current decreases as the anode potential is raised. By comparison of the data on these curves with the curves of Fig. 4, it is seen that they are entirely consistent with the latter.

In looking for an explanation of the shape of these curves, it is important to bear in mind that the lower parts of the curves are determined primarily by the space charge. When the thermionic current is plotted against *temperature*, as in Figs. 1 and 3, the lower part of the curve gives the saturation thermionic current (Richardson), while the upper part gives the part which is limited by the space charge. On the other hand, when we plot the current against the *anode potential*, as in this case, the two parts are interchanged in position; thus the lower part of the curve gives the current as limited by space charge and the upper horizontal part gives the saturation current.

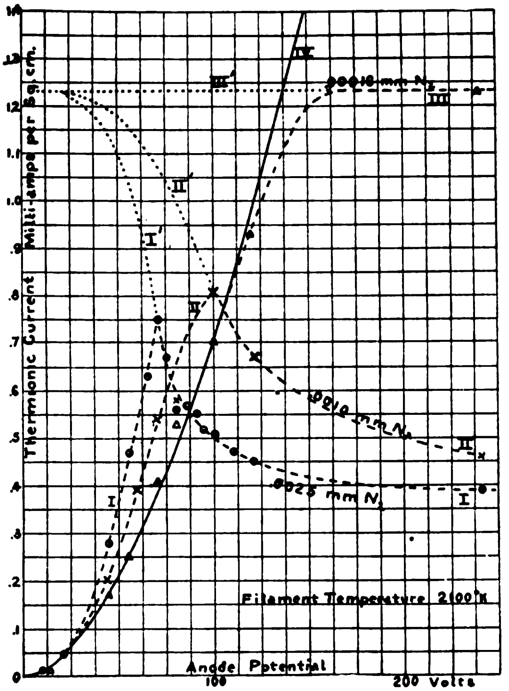

Fig. 5.

The lower part of Curve III., if obtained in a perfect vacuum, should therefore follow equation (11): in other words, the current should increase with $V^{\frac{3}{2}}$. By plotting the first six points of this curve on logarithmic paper, a straight line was obtained, but the slope, instead of giving 3/2 as the exponent of V, gave 1.71. This difference is certainly due to residual gas. Curve IV., Fig. 5, was obtained by continuing the curve

$$i = \text{constant} \times V^{1.71}.$$

The Curve III. separates from IV. above 125 volts because the current gradually reaches saturation for the filament at 2100°.

We are now in a position to discuss the Curves I. and II. At anode potentials below 20 volts the curves seem to coincide fairly well, but the current rapidly increases at higher potentials. Plotting the first six points of Curve I. on logarithmic paper does not give a straight line, but the exponent of V is found to increase from about 2 to over 6. The cause of this rise in current is probably that positive ions are formed by the collisions of the electrons with nitrogen molecules. The positive ions moving slowly carry only a very minute fraction of the current, yet by their mere presence they materially reduce the space charge and therefore allow a larger current to flow.

If this were the only factor, one would expect with increasing voltage that the current would rise to the normal saturation current and then remain constant until the voltage reaches a point where additional electrons are liberated from the cathode by the impact of positive ions against it. But before this point is reached, some other factor begins to make itself felt. This is evidently a limitation of the current not by space charge, but by some phenomenon which prevents the emission of electrons from the cathode. It is, however, not due to a simple alteration of the properties of the material of the cathode, for its magnitude depends on the anode potential.

The following theory seems to be consistent with all the observed facts and may prove to be the correct explanation of the phenomenon.

Theory of the Effect of Nitrogen on the Thermionic Current.—The writer has shown[1] that nitrogen does not react perceptibly with solid tungsten at any temperature, but does react completely with all the tungsten that evaporates from the filament to form the compound WN_2. The evidence indicated that this compound is unstable at temperatures above 2400°. Now although ordinary nitrogen does not react with solid tungsten to form a compound, it is not improbable that nitrogen ions possessing enormously high kinetic energy as compared with the ordinary molecules, will do so. The compound formed, however, being unstable, does not permanently remain on the surface, but either decomposes or volatilizes. Any such process, however, requires a certain amount of time, so that the molecules would remain on or in the surface during perhaps a perceptible fraction of a second. The higher the temperature of the filament, the shorter the average time that would elapse between the formation of a molecule of the compound and its elimination from the surface.

Let us now apply this theory to the data presented in Fig. 5. At an anode potential below 20 volts, no positive ions are formed, so the surface of the tungsten is not exposed to bombardment. At higher voltages the positive ions are produced in increasing numbers and strike the cathode with increasing velocity. As a result the surface becomes more or less completely covered by a layer of molecules of the compound. Since as a rule a compound would be expected to emit electrons less freely than a metal, it is not unreasonable to imagine this surface layer as being the cause of the decreased electron emission.

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[1] Jour. Amer. Chem. Soc., 35, p. 943 (1913).

In a perfect vacuum the actual *electron emission* from the tungsten is independent of the anode voltage as indicated in Curve III'., Fig. 5. However, at low anode voltages the space charge causes most of the electrons to return to the filament, so that the actual *current* obtained is as shown in Curve III. On the other hand, in low pressures of nitrogen the actual electron emission decreases as the anode potential increases, as illustrated by the hypothetical Curves I'. and II'. As in the case of the vacuum, however, at low voltages the space charge causes the return of most of the electrons to the cathode, so that the actual curves (I. and II.) show a current which rises rapidly with increasing potentials. When the potential becomes sufficient to prevent the return of any electrons to the cathode, then the current becomes limited solely by the electron emission from the metal. At high voltages, therefore, the current decreases with increased anode potential because of the increasing proportion of the cathode surface covered with the compound.

The theory thus accounts for the shape of the curves in Fig. 5 in a satisfactory way. It also gives a reason for the shape of the curves obtained with nitrogen given in Fig. 4. The effect of nitrogen has invariably been to greatly decrease the saturation current at 240 volts. At low temperatures this effect is much more pronounced than at high. This is indicated by the fact that the introduction of nitrogen (or oxygen) always increases the value of Richardson's constant b from 55,000 up to 80,000 or more. These facts are in complete accord with the theory, for, as has been pointed out, the length of time that the molecules of the compound will remain on the metal would be much less at high temperatures. Therefore, the higher the temperature, the smaller the proportion of the surface covered by molecules of the compound, and the nearer the observed thermionic current approaches the normal saturation current.

Whatever the nature of change in the surface of the tungsten which decreases the electron emission, it is one which does not persist for more than a few seconds after the removal of the nitrogen. In the course of all these experiments, except before ageing the filaments, there were never any effects which could not be immediately duplicated after interchanging the functions of the two electrodes. There is therefore no reason to call upon any "inexhaustible supply of gas" in the filament to account for any of the phenomena observed.[1]

Effect of Anode Potential at Higher Filament Temperature.—The data on the effect of anode potential obtained with the filament at a higher temperature, 2300° K., is given in Fig. 6. With .0010 mm. of nitrogen, the current rose steadily (Curve I.) until a potential of about 135 volts was reached. With potentials higher than this, the current would rise to a high value, .013 amp. per sq. cm. or more, immediately on lighting the filament, and the discharge was accompanied by a strong purple glow filling the bulb. Suddenly the current fell to .005 amp. per sq. cm. or less, and at the same time the purple glow vanished. Every time that this happened the pressure in the system would fall to from about .0012 to .0006 or less, so that fresh nitrogen had to be admitted after each trial.

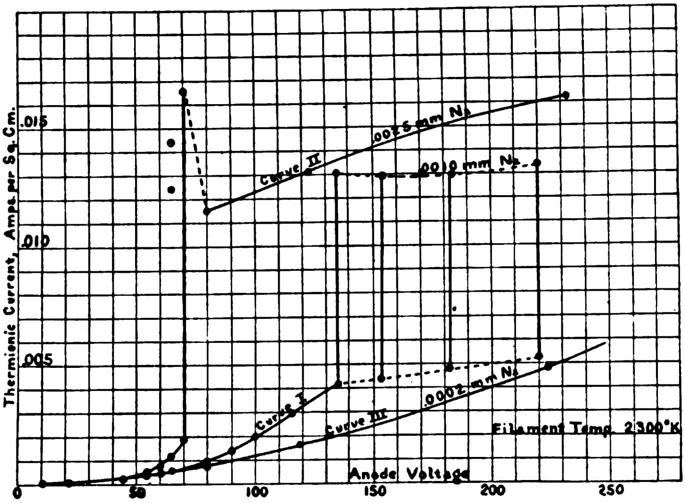

Fig. 6.

With a pressure of about 0.0025 mm. of nitrogen (Curve II.) a discontinuity occurred in the current values at an anode potential of 70 volts. Above this, however, the current was again steady. These unstable conditions are probably due to ionization reaching such a value that the bombardment of the cathode by the positive ions gives rise to additional electrons. These in turn cause the formation of fresh positive ions. The effect is thus one which can readily become unstable. It is interesting to note, however, that even with this additional electron emission, the current is still less than the *saturation* current in a perfect vacuum, which from Curve I'., Fig. 4, would be about .050 ampere per sq. cm. Undoubtedly at higher pressures and voltages than those used the currents caused by ionization would ultimately greatly exceed the saturation current from the filament.

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[1] The writer feels strongly that the majority of the cases cited in the literature where fine platinum wires, etc., apparently continue to give off gas after prolonged heating, are caused not by gas from the wire, but by water vapor or other gases liberated from the walls (or vapors from stopcock grease or sealing-wax) which are changed chemically by the hot wire or by electrical discharges.

Curve III. gives the current obtained with a much better vacuum and probably represents very closely the normal current as limited by space charge. The effect of the nitrogen is thus mainly to produce positive ions and neutralize the space charge.

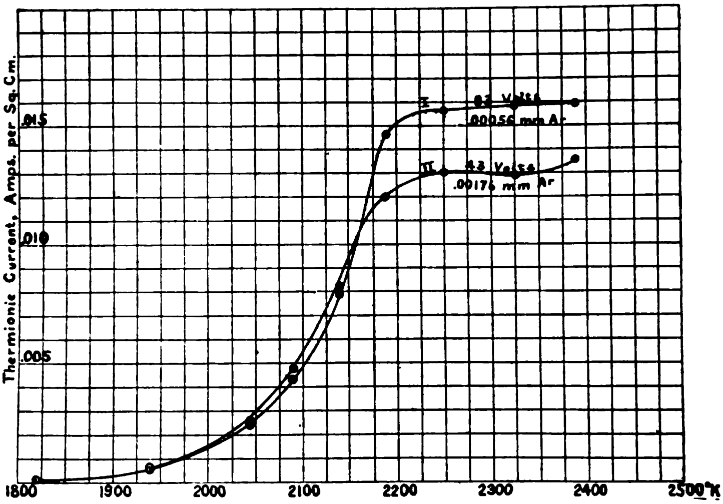

Fig. 7.

Argon.—A series of experiments was made to determine the thermionic current in low pressures of argon. The surprising result was obtained that the saturation currents were in every case (pressures up to .002 mm.) identical with the results previously obtained in the best vacuum. That the argon had the further effect of neutralizing the space charge is shown by the relatively large currents obtained with anode voltages of only 40–100 volts.

In all, about thirty runs were made, and with two exceptions they all gave values of the Richardson constant *b* between 50,500 and 58,000. The Curves I. and II., Fig. 7, are examples of typical runs. It is seen by comparison with Fig. 3 that the maximum currents obtained are considerably larger than those to be had in vacuum with similar voltages, but these larger currents are due solely to the removal of the limitation imposed by the space charge. At lower temperatures the currents obtained are practically identical with those in vacuum.

Another remarkable fact about the effect of argon on the thermionic current is that considerable admixtures of nitrogen or even oxygen have little or no effect. Thus, while the filament was running at 2190° in argon at .0016 mm. pressure, an amount of nitrogen was let in, which raised the pressure to .0035, yet the current at 240 volts changed only about 5 per cent.

In another case, while the filament was running under similar conditions as in the test with nitrogen, an amount of oxygen was suddenly admitted sufficient to raise the total pressure from 0.0016 to 0.0035 mm. In this case the current was decreased by about 10 per cent. for a few seconds, but rapidly returned within a couple of per cent. of the original value. Upon lowering the temperature to 2045°, the thermionic current was found to be only 7 per cent. of its value in argon, while at 2140° it was 20 per cent. of its original value. If these results are compared with those cited previously on the effect of oxygen on the thermionic current, it will be seen that the argon has enormously weakened the effect produced by oxygen, especially at higher temperatures.

Argon acted remarkably in another respect. The thermionic current in argon caused very marked disintegration of the hot cathode; whereas this effect is entirely absent in a good vacuum with a pure electron current, and only present to a very slight degree in pressures of nitrogen as low as .002 mm. With the argon the filament rapidly increased in resistance by loss of material which deposited on the bulb in the form of black bands, principally behind the *anode*. These bands had more or less the shape of the anode filament and had a white strip down their centers —evidently the shadow cast by the anode. This proves that the tungsten which was sputtered from the cathode was or became *negatively* charged. It is surprising that the thermionic current was identical with that in a high vacuum, notwithstanding this marked disintegration of the cathode. This experiment certainly proves that there is no necessary relation between cathodic disintegration and thermionic current.

These results with argon are strong support for the theory that the positive ions of nitrogen or ordinary molecules of oxygen form unstable compounds with the tungsten which prevent the normal electron emission. Argon not being capable of reacting chemically with the tungsten does not reduce the thermionic currents.

The explanation of the action of argon in preventing oxygen and nitrogen from having their normal effect is probably that the bombardment of the cathode by the positive argon ions, which is undoubtedly (in accordance with Stark's theory) the cause of the sputtering of the cathode, also sputters away any compound formed and thus keeps the surface of the tungsten clean. At lower temperatures and hence lower currents, the sputtering is less marked and therefore the argon interferes less with the normal action of the oxygen.

EXPERIMENTS WITH PLATES AND CYLINDERS AS ANODES.

In all the experiments mentioned thus far, the anode has been a tungsten filament which has been freed from gas by heating to 2500°. Several experiments, however, were also made with anodes of thin sheet metal, in the form of plates or cylinders. In general, in these experiments, unless very special methods of treating the electrodes are adopted, the evidences of the presence of gas are much more marked than in the experiments with filaments as anodes. A great variety of erratic effects occur, such as gradual changes in the thermionic current, and various kinds of fatigue effects. Some of these effects are particularly pronounced at low temperatures of the filament. A large amount of data has been obtained in studying these effects, and much of it is of such interest that the results will be published in detail in subsequent papers. For the present it will suffice to consider the results of a few runs at various filament temperatures and anode voltages, in a lamp containing a cylindrical anode.

The anode in this experiment consisted of a cylinder of platinum foil, 3.5 cm. diameter and 6 cm. long. Inside of this, about 1 cm. apart, were placed two single loop tungsten filaments of wire .0127 cm. diameter and each 9.9 cm. long. The surface of each was thus 0.40 sq. cm. A cylindrical glass bulb fitted closely about the platinum cylinder.

The platinum cylinder, before placing in the lamp bulb, was ignited for a few minutes over a blast lamp to a white heat and washed with nitric acid, but other than this, purposely not subjected to special treatment.

This lamp was sealed to the same system as before and the same care was used in exhausting it as in the other experiments. That is, after exhausting to 0.001 mm., the bulb was heated to 370° C. for an hour and a half. From the beginning to the end of the experiment the trap directly below the lamp was kept in liquid air.

During the first few days the results were extremely erratic and were characterized especially by lag or fatigue effects. The results showed clearly, however, that these were not due to gas contained in the filament, but were rather caused by gas from the anode liberated by electron bombardment. The quantities of gas liberated, however, were very small, so that even with the Töpler pump no great difficulty was experienced in keeping the pressure continually below .001 mm.

The runs about to be described were made on the tenth day after the beginning of the experiment. By this time most of the erratic effects had disappeared and the results obtained were beautifully reproducible.

A series of runs was made with the following anode voltages, and in the following order: 240, 124, 30, 50, 70, 90, 70, 50, 30, 20, 110, 124. At each voltage the thermionic currents were measured at temperatures from 1850° to 2350 or 2500°, in steps of 50°. The pressure during all these runs varied within the limits .00007 to .00023 mm. In every case different runs at the same anode voltage gave practically identical results. Furthermore, at temperatures so low that saturation current was obtained, the thermionic currents at different voltages were the same.

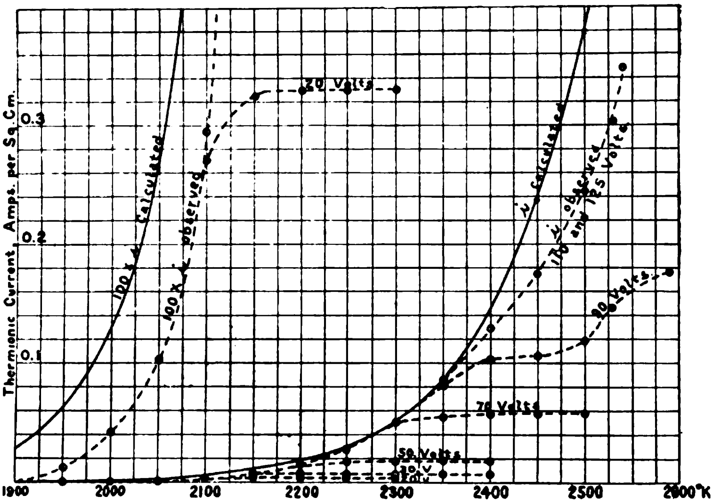

Fig. 8.

The results of these runs are given in Fig. 8. All the experimentally determined points are given, except where the curves run together, and then the points for the curve made at 110 volts are given.

For comparison with these results, the Curve I., of Fig. 3, has been replotted in Fig. 8 (continuous heavy line). This curve gives the results that were obtained under good conditions in a vacuum and in a case in which temperatures were determined in the same manner as in the present experiment.

The upper portion of the curve (not given in Fig. 3) was calculated by Richardson's equation, using the constants

$$a = 34 \times 10^6,$$

$$b = 55{,}500.$$

It will be seen, from Fig. 8, that the currents obtained with the cylindrical anode are much larger than any recorded previously in this paper. Thus with 110 volts or more, currents up to 0.350 ampere per sq. cm. (actual current measured was 0.139 amp.) were obtained. But the curves show plainly that at the *same temperature* of the filament, the currents are always less than those obtained under the best vacuum conditions. The shape of the anode reduces the effect of space charge and thus allows much more current to flow with the same voltage than in the previous experiments.

This experiment offers the most convincing evidence possible of the correctness of the general theory of the effects of gas outlined previously.

According to this theory, the effect of certain gases (probably most gases except the inert gases) is to *cut down* the normal electron emission from the heated metal, by the formation of an unstable compound on the surface. At higher temperatures the rate of decomposition or evaporation of the compound is greater and hence fewer molecules of the compound remain on the surface. At sufficiently high temperatures the compound should completely disappear and thus allow the electron emission to become normal.

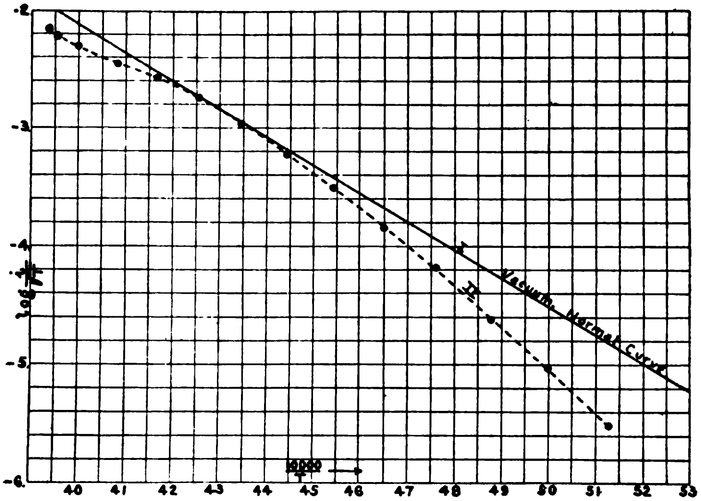

Fig. 9.

The present experiment is in full accord with this theory. At low temperatures the electron emission (saturation current) is much less than the normal, but at higher temperatures it increases rapidly up to the normal value, but the current *never exceeds the normal current.*

These facts are made much clearer by plotting log $i/\sqrt{T}$ against $1/T$ (Fig. 9). With these functions as coördinates, the points should lie on a straight line if the current follows Richardson's equation. Curve I. is the normal vacuum curve shown in Figs. 3 and 8, and Curve II. is that obtained from the experiment with the cylindrical anode at a potential of 110 volts. It is seen that the second line is not straight. The lower part is practically straight, but the upper part *does not cross* the normal vacuum curve, but instead bends over and joins it. The reason that it does not follow it at higher temperatures, is probably that space charge is having some effect, as in the run with 90 volts (see Fig. 8). The *extremely* close coincidence between the observed and calculated curves over the short range of contact is undoubtedly partly accidental.

The fact that the curves obtained at low anode voltages (20–30 volts) coincide at lower temperatures with the curves obtained with high potentials, show in this case that the compound on the surface is not formed from positive ions, but is formed directly by a reaction between the gas and the metal. The gas in this case is probably carbon monoxide or hydrogen, and can easily be supposed to react in this way to form unstable compounds. With nitrogen, on the other hand, the evidence is good that the compound only forms when positive nitrogen ions strike the filament.

The effect of the gas in eliminating the space charge is strikingly shown in this experiment. At higher potentials the thermionic current increases much more rapidly than the three halves power of the voltage. This shows that positive ions are formed which reduce or eliminate the space charge produced by the electrons, yet themselves do not carry a perceptible portion of current.

Some other experiments, to be described in detail in a subsequent paper, have shown, that the bombardment of the cathode even by positive ions of a velocity corresponding to only 110 volts, causes the cathode to emit electrons having a velocity corresponding to a velocity of 6–12 volts. Thus a third filament in a bulb in which a thermionic current is flowing often charges up rapidly to a potential of 10 volts *negative* with respect to the *negative* end of the cathode filament. This observation is entirely in line with previous observations on delta rays and electron emission caused by canal rays.

GENERAL DISCUSSION.

The evidence presented in this paper and the theories that have been advanced are thought to throw a rather new light on the electron emission from incandescent solids in high vacuum.

In the first place, the work indicates that the experimental conditions that have commonly been employed in the investigation of thermionic currents in vacuo have not been well adapted to eliminate important secondary effects. The proper conditions seem to be:

1. Extremely high vacuum; that is, a pressure below .0001 mm. should be obtained. The presence of certain gases is much more injurious than others. Gases such as oxygen, water vapor, carbon dioxide, and hydrocarbons, which are very active chemically at high temperatures, should be especially avoided. This means that all stopcocks and sealing-wax must be eliminated and all glass parts not to be cooled by liquid air must be heated for at least an hour to 360° or more. Even with the Gaede molecular pump these precautions are necessary.

2. Avoidance of large anodes, except those that have been especially treated by heating in a vacuum to 2000° or have been exposed to powerful electron bombardment in a very high vacuum. Treating the metal by making it an electrode in an ordinary glow discharge, except when the inert gases are used, is about the worst thing that could be done to it. Preferably the anode should consist of tungsten wire which is freed from gas by heating to 2500° for ten minutes. This should be done in the apparatus itself.

3. The relative position and size of the electrodes should be such that space charge does not limit the current to an undesirable degree.

If proper precautions are taken to obtain an extremely high vacuum, and if the anode consists of molybdenum or tungsten and is given a preliminary treatment by exposing to very powerful electron bombardment, it is possible to use cylindrical anodes without obtaining the slightest evidence of positive ionization. For this purpose the anode should be charged to several thousand volts and the filaments raised to such temperatures that 50–200 milliamperes thermionic current are obtained. Under these conditions the anode becomes heated to a bright red or white heat, and the combined effect of the electron bombardment and the high temperature is to free the anode from gas. After such treatment pure electron currents of several tenths of an ampere may be obtained without positive ionization. Dr. Dushman has found that under these conditions the space charge equation (20) holds with a high degree of accuracy.[1] In this way, by using three cylindrical anodes on the guard ring principle, it should be possible to use equation (20) to determine the value of e/m with a degree of precision greater than that obtainable by any other method. Neither the writer nor Dr. Dushman intends to make such precision measurements and therefore we would like to suggest that this method be seriously considered by those who plan to make such determinations.

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[1] These results will soon be published by Dr. Dushman.

Failure to observe the conditions given above has, it is feared by the writer, very seriously vitiated most of the quantitative results obtained in the past on thermionic current in a vacuum. It is also undoubtedly the principal cause of the opinion which is so prevalent today that the electron emission from hot solids is a secondary effect, probably usually produced by chemical reactions, which would disappear if a perfect vacuum could be obtained.

The evidence presented in this paper will, it is hoped, counteract these unfortunate tendencies and help place the Richardson theory of electron emission on a firm footing or at least stimulate the critical study of the theory. The thermionic effect is of at least as great intrinsic interest as the photoelectric effect, and should receive as much, if not more, attention on the part of physicists.

Let us now examine more closely some of the experiments which have led to the common knowledge of thermionic currents in vacuo.

With platinum wires extremely variable results have been obtained. H. A. Wilson found that by heating the wire in oxygen or by previously boiling it for 24 hours in nitric acid, the thermionic current would be reduced to the 100,000th part of its original value. This lower value, however, he considers the normal value in a vacuum, and believes the increase observed when hydrogen is admitted to be due to some secondary effect.

The effect of oxygen on the thermionic current from platinum is so strikingly similar to that observed with tungsten that the writer cannot help but feel that the cause in both cases is similar. The writer has found,[1] and will soon publish his results in detail, that when a platinum wire is heated in oxygen at low pressure, the platinum evaporates at the *same rate* as in a vacuum and that the platinum *vapor* combines quantitatively with the oxygen after it leaves the surface of the wire to form the compound PtO_2. This is identically the same type of reaction that has been observed with tungsten and nitrogen. This suggests strongly that oxygen would have a similar effect on the thermionic current from platinum that nitrogen has on tungsten. In other words, the oxygen would cut the thermionic current down to a value *lower* than the normal vacuum current. Hydrogen would reduce the oxide and allow the normal current to flow. Of course it is quite possible, although not probable, that some gases may increase the thermionic current instead of decreasing it.

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[1] Jour. Amer. Chem. Soc., *35*, p. 944 (1913).

PRING AND PARKER'S EXPERIMENTS.[1]

The excellent experiments of these investigators have been perhaps the most convincing evidence that the thermionic electron emission is a secondary effect. Let us therefore criticize the experiment in the light of the new theory.

In the first place, carbon is a substance which at high temperatures is particularly active chemically, so that it probably reacts with every gas present in the system. The residual gases may therefore be expected to have a particularly strong action in reducing (or possibly increasing) the thermionic current. Although Pring and Parker have attempted to obtain a high vacuum, and have measured the pressures, yet the best vacuum they claim to have attained, while heating the cathode, is .001 mm. Actually, however, the pressure must have been at least several times this amount, for mercury vapor (.002 mm.) had free access to the apparatus and they used "soft wax" in several places, which gives off large quantities of various vapors, all of which are readily condensible and therefore not indicated by the McLeod gage.

In the second place, the distance between anode and cathode in their experiments varied from 4.8 to 11 cm., so that in a perfect vacuum, with only 330 volts on the anode, they could have obtained only very little current because of the space charge. For example, if we calculate from equation (11) the total current that could be carried at 330 volts between two electrodes 8.0 cm. in area at a distance of 4.8 cm., we obtain only .0048 ampere. Whereas Pring and Parker obtained currents as high as 40 amperes, with only 40 to 60 volts in the beginning; later on, after the carbon had ceased giving off large quantities of gas, the currents fell to as low as .000016, with the temperature of the carbon rod at 2050°.

The reason that the currents in their experiments went down to values so much below that which we have calculated above from the "space charge" equation may possibly be that the electron emission was actually decreased to that low value by the presence of gas. A much more probable explanation suggests itself by referring to the diagram of their apparatus (Fig. 1, Pring and Parker's paper). Apparently they have placed a glass cylinder, *F*, around the anode, in order to protect the walls of the tube from the radiation from the hot anode. In discharges at high pressures this cylinder would have little or no effect on the discharge, but at low pressures, where the free path of the electrons from the cathode becomes commensurate with the distance (apparently about 2 cm.) from the cathode to this cylinder, the effect is very important. At very low pressures these electrons charge up the cylinder to the potential of the anode and therefore practically destroy the potential gradient close to the cathode, where it is especially needed to remove the space charge. The writer has often observed effects of this kind in connection with his work: in fact, in very high vacuum the charging up of the glass sometimes becomes very troublesome. Thus, in some cases, after measuring a thermionic current with 240 volts on the anode, no current at all will be obtained when the anode potential is changed to 120 volts. By touching the bulb with the hand and then with the other hand touching the positive terminal of the direct current supply line, the current instantly starts up again.

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[1] Phil. Mag., *23*, 192 (1912).

In Parker and Pring's experiments, therefore, as the vacuum improved, the potential available for the removal of the space charge decreased very rapidly, and this effect is probably responsible for the extremely small currents obtained by them in some cases.[1]

Lilienfeld's Experiments.[2]

Lilienfeld has concluded from the results of very careful and elaborate experiments in which we took precautions to obtain a particularly high vacuum, that positive ions play an essential rôle in conduction of electricity, even through the highest vacuum. He finds that beyond a certain point these effects are entirely independent of the degree of vacuum. He finds also that the potential gradient is uniform in the space between the electrodes and that the current varies almost exactly proportional to the *square* of the potential gradient. He shows from these results that there is no space charge (except at extremely low currents), but that there must be equal numbers of positive and negative ions in every unit of volume.

Lilienfeld used a Wehnelt cathode as a source of electrons, and anodes of platinum foil, which were kept cold by liquid air while the discharge passed.

These results are so radically different from those that have been described in the present paper, that they call for comment. The effects observed by Lilienfeld are certainly real, and prove that the kind of discharge that he was studying is totally distinct from the pure electron currents that have been obtained with hot tungsten cathodes.

The essential difference in the conditions is undoubtedly the use of the Wehnelt cathode.

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[1] In still more recent work Pring (Proc. Roy. Soc., *89*, 344, 1913) again finds the electron emission from carbon to be due entirely to secondary effects. Undoubtedly the large currents that have often been obtained are due to these causes, but some measurements we have made show clearly the existence of a true electron emission. (See Appendix).

[2] Ann. Phys., *32*, 673 (1910).

From some experiments made in this laboratory with Wehnelt cathodes, and judging from the experiments of Child[1] the writer is strongly of the opinion that the Wehnelt cathode is not a primary source of electrons at all, but is simply a cathode which is particularly sensitive to bombardment by positive ions and under the influence of such bombardment emits electrons copiously.

In Lilienfeld's experiments, with the long and crooked path between anode and cathode, the space charge would have prevented a pure electron discharge from taking place. The Wehnelt cathode, however, probably liberates quantities of gas sufficient to furnish the positive ions necessary. It is also possible that Lilienfeld obtained a steady evolution of sufficient gas by the electron bombardment of the anodes which had never been properly freed from gas.

APPENDIX.[2]

Since the foregoing paper was written, a large amount of data on thermionic currents from various metals have been obtained under conditions of still better vacuum. The measurements thus far made are of a preliminary nature, but seem to indicate that the normal thermionic current from tungsten is even larger than that previously given. Much more accurate determinations of the thermionic currents from tungsten, tantalum, molybdenum, platinum and carbon are in progress, and will be published. The results thus far show that with all these substances, the effect of residual gases is always to decrease the thermionic current. Often the current obtained after the best vacuum conditions have been attained is 100–1,000 times as great as that observed when only the usual means of obtaining so-called high vacuum are employed.

The following preliminary results, giving the observed thermionic currents in milliamperes per sq. cm. from various filaments at 2000° K., may be of interest, but should be considered merely as lower limits to the normal electron emission in a perfect vacuum:

Metal.	Thermionic Current at 2000° K. Milliamps. per Sq. Cm.	Richardson's Constant b.
Tungsten	3	55,000
Tantalum	7	50,000
Molybdenum	13	50,000
Platinum	0.6	80,000
Carbon	1.0	32,000

The values of b given in the last column are probably all slightly too high. With platinum it is extremely difficult to get concordant results, probably because the surface film is fairly stable, even close to the melting-point of the metal. Fredenhagen[1] has recently given reasons for concluding that none of the measurements thus far made of thermionic currents from platinum have really given anything more than secondary effects. He suggests that the presence of an oxide film may seriously affect the results. Our experience has fully confirmed his conclusions.

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[1] PHYS. REV., 32, 492 (1911).

[2] Added during correction of proof.

Summary.

It is shown both theoretically and experimentally that the mutual repulsion of electrons (space charge) in a space devoid of positive ions, limits the current that flows from a hot cathode to a cold anode. For parallel plane electrodes of infinite extent, separated by the distance x, and with a potential difference V between them, the maximum current (per unit area) that can flow if no positive ions are present is

$$i = \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{x^2}.$$

For the analogous case of an infinitely long, hot wire, placed concentrically within a cylindrical anode, of radius r, the maximum current per unit length is

$$i = \frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{V^{\frac{3}{2}}}{r\beta^2},$$

where β varies from 0 to 1, according to the diameter of the wire, but for all wires less than 1/20 the diameter of the anode, β is a quantity extremely close to unity.

2. In the presence of gas at pressures above .001 mm., and at voltages above 40 volts, there is usually sufficient production of positive ions to greatly reduce the space charge and thus allow more current to flow than indicated by the above equations.

3. It is shown, contrary to the ordinary opinion, that the general effect of very low pressures of gas is to greatly *reduce* the electron emission from an incandescent metal.

4. This effect is especially marked at low temperatures. In most cases it probably disappears at very high temperatures.

5. The constant b of Richardson's equation

$$i = a\sqrt{T}e^{-\frac{b}{T}}$$

is always increased, in the case of tungsten, by the introduction of oxygen, nitrogen, water vapor, carbon monoxide or dioxide. Argon, however, has no effect on either constant.

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[1] Leipziger Berichte, math. phys. Kl., 65, 42, 1913.

6. The normal thermionic current from tungsten in a "*perfect*" vacuum follows Richardson's equation accurately. The constants approximately:

$$a = 34 \times 10^6 \text{ amps. per sq. cm.},$$

$$b = 55{,}500.$$

7. Preliminary data are given for the electron emission from tantalum, molybdenum, platinum and carbon. With these substances also the effect of gases is to greatly decrease the electron emission.

8. The effect of nitrogen in decreasing the thermionic current from tungsten depends on the voltage of the anode. In many cases less current is obtained with 240 volts than with 120 volts. With oxygen, the effect seems independent of the anode voltage.

9. The following theory seems to account for most of the observed phenomena and is apparently not inconsistent with any:

The effect of gases in changing the saturation current is due to the formation of unstable compounds on the surface of the wire. In the cases observed the presence of the compound decreases the electron emission. It is possible, however, that in some cases it might cause an increase. The extent to which the surface is covered by the compound depends on the rate of formation of the compound and on its rate of removal from the surface. The compound may be *formed* on the surface directly by reaction with the gas (for example, oxygen), or by reacting principally with positive ions which strike the surface (nitrogen). The compound may be *removed* from the surface by decomposition, evaporation, or cathodic sputtering (*i. e.*, being driven off by bombardment of positive ions).

10. The experimental conditions which should be met, in order to most easily study the thermionic currents in high vacuum, are discussed. It is pointed out that failure to observe these conditions is probably the cause of other investigators' having found that the thermionic currents tend to decrease with increasing purity of the cathode and progressive improvement of the vacuum.

11. It is concluded that with proper precautions the emission of electrons from an incandescent solid in a very high vacuum (pressures below $.10^{-6}$ mm.) is an important specific property of the substance and is not due to secondary causes.

In conclusion the writer wishes to express his appreciation of the valuable assistance of Mr. S. P. Sweetser, and Mr. William Rogers who have carried out most of the experimental part of this investigation.

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THE SENSIBILITY CURVES FOR SELENIUM; A NEW SENSIBILITY-WAVE-LENGTH MAXIMUM AND A NEW PRINCIPLE.

By F. C. Brown and L. P. Sieg.

RECENTLY Pfund[1] found a maximum in selenium at wave-length 690 $\mu\mu$ which disappeared when the intensity of illumination became very faint. This disappearance calls attention to the complexity of the light action in selenium. The present authors were led to believe as a result of a mathematical analysis that the complex behavior might be simplified by using very short periods of exposure to the light, and even that the maxima might disappear for intense illumination also. We have been surprised to find in the Giltay cell a very pronounced maximum at 800 $\mu\mu$, which disappears with small intensity just as the maximum discovered by Pfund in the region of 690 $\mu\mu$ was observed to vanish. And further, not only does this maximum disappear with intense illumination when the selenium is exposed for a short interval of time, but all maxima disappear, such that the remarkable result is obtained that the change of resistance of the particular cell studied is independent of the wave-length of the incident light between 460 and 790 $\mu\mu$. The change of resistance for light in this region is solely a function of the intensity. This last conclusion is important in that it promises us an instrument for measuring energy in the visible spectrum more delicate than the thermopile or bolometer. In this article we propose to restate the conditions under which the maxima appear and to define a method of using the selenium cell for energy comparisons of the various wave-lengths in the visible spectrum.

Theory.

First we wish to make clear that for intense illumination made up of all visible wave-lengths, we should obtain the simplest conditions by using short exposures. A mathematical analysis has revealed[2] that for the Giltay cell when exposed to approximately white light there are two direct and two reverse changes taking place and only one conducting element. On p. 408 of the article referred to are given the rates of change and the constituents of the cell under specified conditions. For a short exposure at 18° C. the changes in the conductivity are made up relatively as follows:

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[1] Phys. Rev., XXXIV., p. 370, 1912.

[2] See paper by F. C. Brown, Phys. Rev., 33, p. 403, 1911.

$$\begin{array}{lllrcll}
A \rightarrow B = \alpha_1 A = & 11,200 & \times & .054 & = & 604 \\
A \leftarrow B = \alpha_2 B = & .8 & \times & 12 & = & 9.6 \\
B \rightarrow C = \beta_1 B = & .8 & \times & .9 & = & 0.7 \\
B \leftarrow C = \beta_2 C = & 3.6 & \times & .004 & = & 0.0
\end{array}$$

Thus it appears that we obtain appreciable changes only between the A and B components, and of these the direct change constitutes about 98 per cent. of the total. But for long periods of exposure the amount of each of the four changes above noted approaches equality, as A becomes less, and B and C become greater. The analysis shows therefore that the short exposure gives simple and single changes, while any long exposure gives a most complex and varying summation, because the amounts of A, B and C are continually changing with time. Maxima obtained for long exposure really have very little meaning until we first establish what part of the maximum can be sorted out and attributed to the direct change from A to B.

But aside from what has just been said, short exposures should give a constant change, because for a short interval the amounts of the A, B, and C components are approximately fixed, and since the rates of change are unvarying under given conditions, the sum of $\alpha_1 A - \alpha_2 B - \beta_1 B + \beta_2 C$ should be constant. For any long interval the interchange of the components makes the process very complex.

We therefore decided to map out the sensibility of the selenium for equal energy throughout the spectrum, by exposing the selenium for only a fraction of a second, using sensibility curves for longer exposure merely for comparison.

There is nothing so far in the theory to indicate why short exposures should or should not give sharp maxima. Short exposures however should give simple conditions.

ARRANGEMENT OF APPARATUS AND METHOD OF MEASUREMENT.

To obtain the sensibility curves, the principle laid down by Pfund[1] was followed. The change of resistance for equal energy was measured throughout the visible spectrum. The arrangement of apparatus is shown in Fig. 1. Light from a Nernst filament, N, manufactured by Pye and Co. for their lamp and scale outfit, is focused by the lens L, on the collimating slit S_1 of a constant deviation monochromatic illuminator, manufactured by Spindler and Hoyer. The Nernst glower was maintained at constant intensity by using storage battery for heating current. The bundle of quasi-homogeneous rays was then focused on the slit S_2, and from there was focused by means of the concave mirror M, upon either the thermopile slit or the selenium cell, as desired. The lenses of the monochromatic illuminator were 20 mm., or $f/12.7$ in diameter, and hence with this apparatus, much of the energy is lost. A new illuminator of greater light-gathering power has been obtained and will be used for future work. The slits S_1 and S_2 were kept of equal width, which varied from 0.2 to 1 mm. The length of the slits was one centimeter.

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[1] Phil. Mag., Jan., 1904.

The thermopile was of the Rubens type, but it was of bismuth-silver wires of the improved design of Dr. W. W. Coblentz. It was remarkably free from drift and altogether very satisfactory, as used with a Thomson galvanometer made by Siemens & Halske. The galvanometer had a resistance of 5.4 ohms, and the thermopile had a resistance of 7.4 ohms. This combination when a glass cover was in front of the thermopile junctions gave a deflection of 300 divisions with a candle at a meter. The period was about 5 seconds for this sensibility. By increasing the period the sensibility could have been increased several times, easily to more than 1,000 divisions per candle per meter.[1]

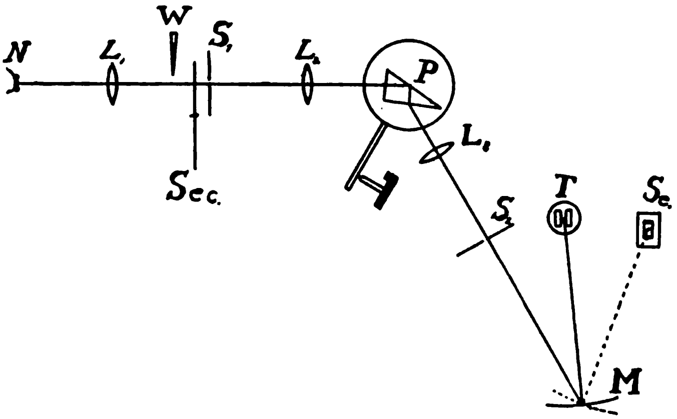

Fig. 1.

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[1] Since the above test was made we have received a standard carbon incandescent lamp from the Bureau of Standards, calibrated for total radiation in a given direction. By means of this standard lamp we found the sensibility of the thermopile to be 9.3×10^{-8} watts/mm. deflection on our scale. It must be remembered that this sensibility was obtained with a glass cover over the thermopile. Had this cover been removed, the sensibility would have been much greater.

A Giltay cell, the one previously studied by one of the authors, was used.[1] It had a resistance of 299,000 ohms in the dark with 4 volts in the circuit, or 270,000 ohms with 20 volts. It was connected in a Wheatstone bridge. For the long exposures a potential of 4 volts was left in the circuit continuously, but for the exposures of a fraction of a second duration the potential was changed to 20 volts. During the experiments the temperature did not vary from 24° by as much as one degree. For the long exposures a Leeds & Northrup high sensibility galvanometer of about 1,000 ohms was used. For the short exposures the method outlined by Brown and Clark[2] was adopted. With this a ballistic galvanometer of 22 seconds period was substituted for the above galvanometer.

We deviated from the procedure outlined by Dr. Pfund in two essentials. An exposure of a fraction of a second was used, and secondly we did not give the cell a special treatment of the nature of preliminary exposure before making each observation. Aside from the advantage of simplifying the conditions, the short exposure has the advantage in that a shorter time is necessary for recovery. We do not believe in the special treatment immediately before making an observation, because such only exaggerates the complexity, and makes it more difficult to define the characteristics of a given sample of selenium. Each distinct preliminary treatment should give a corresponding distinct sensibility curve, providing only that the special treatment varies either in duration or nature of action on the slow rates of change in the selenium.

The intensity of illumination was varied by a rotating sector disc, *Sec*, and an optical wedge, *W*, (Fig. 1) either singly or in combination. It was very easy by this combination to verify the applicability of Talbot's law. However we did not make as extensive a verification as was made by Pfund.

The total area of the selenium exposed was about 4 mm^2, which was only a little more than a thousandth part of the entire sensitive surface. The fact that only such a small portion of the selenium was exposed was marked only by an apparent decrease of the sensibility of the selenium by a constant value.

We first obtained a family of sensibility curves with varying energy intensity on the selenium using long periods of exposure, 30 sec. In general the energy on the thermopile was adjusted to constant deflection of the galvanometer (20 div.) or to within five per cent. of this value. Then the selenium was exposed to this same bundle of energy. The slit width was 0.2 mm. This width gave a very sharp maximum (see

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[1] PHYS. REV., 33, p. 403.

[2] PHYS. REV., 33, p. 53, 1911.

Fig. 2) at 800 μμ, a maximum less sharp and much less pronounced at 690 μμ, and a broad maximum extending from 540 μμ to 600 μμ (Fig. 2). In obtaining Curve *C* a different practice was resorted to. First the energy from a Nernst glower was measured throughout the spectrum. And then to obtain equal energy on the selenium the calibrated sector disc openings were adjusted in inverse ratio to the energy in the different parts of the spectrum. This method had the advantage of picking out the characteristics of the curve quickly and with a small number of observations, but it required supplementary readings by the other method in some instances in order to obtain higher precision in the relative values of adjacent points. The energy intensity which gave curve *A* was about that of a candle at four meters. The intensity of exposure on the selenium was decreased by use of the sector disc by steps, until it was diminished to one fortieth of the above value. The curves are shown in Fig. 2.

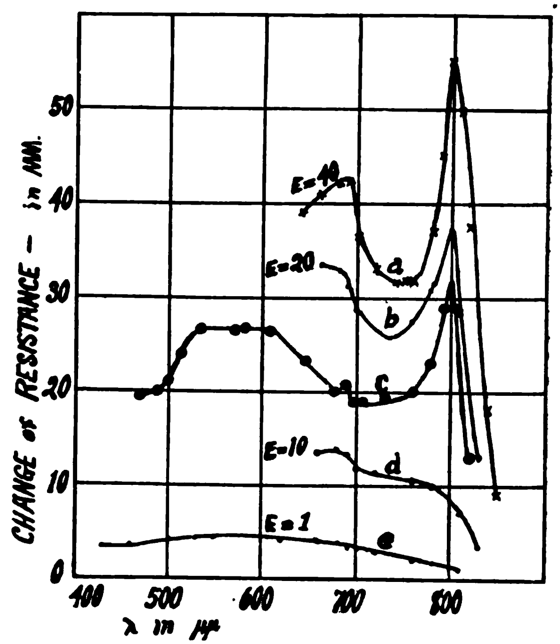

Fig. 2.

The points of interest are first that there is a sharp maximum at 800 μμ which has not hitherto been observed in selenium, and second that faint energy will not bring out this maximum. This last point is very similar to Pfund's observation. The vanishing of the maxima with faint illumination may be explained in terms of the rates of change existent in selenium. For faint illumination all the rates of change are small, particularly are α_1 and α_2 small in comparison with their values for intense illumination. This simply means that in a 30-second interval with faint illumination there is only time for the *A* component to be transformed into the *B* component and of the original *B* component to be transformed into the *C* component, and that of the *B* component for example the excess formed by the light is so small in this time that only the original amount need be considered in the formation of the *C* component. A long exposure to faint illumination tends to approach the same simplicity that a short exposure to intense illumination accomplishes.

We next tested the effect of varying the time of exposure to intense light referred to in the theory to see if the maximum would tend to vanish. The new duration of exposure was .4 sec. and the slit width was one millimeter. The energy beam was focused on the selenium, so that we obtained a somewhat greater energy intensity than any which gave the curves in Fig. 2. The observations were found to agree with each other very well indeed; five observations were taken for each setting of the illuminator except one. One division on the scale was usually the maximum variation obtained. For the selenium the error was not as great as one per cent. However it was not easy to assure the individual thermopile readings to a greater accuracy than five per cent.

The Curve *A* (Fig. 3) shows the average of the deflections of the ballistic galvanometer, *i. e.*, the change of resistance, between 500 $\mu\mu$ and 810 $\mu\mu$. It is altogether probable that the single point that is off the curve was off as a result of error due to insufficient number of thermopile readings. By the method that we used it was necessary to diminish the energy in order to make observations beyond 500 $\mu\mu$. By diminishing the energy to 1/20 of the original value the Curve A_2 was obtained. The average of a large number of observations indicated that the independent relationship between wave-length and deflection extended back as far as 460 $\mu\mu$.

The Curves *B* and *C* represent the observations for long periods of exposure to the same intensity as above mentioned. The ordinates for Curves *B* and *C* are arbitrary and do not correspond to those for Curve *A*. It is observed that a 60-second exposure (Curve *C*) makes the maxima and minima slightly more pronounced than a 30-second exposure (Curve *B*). Perhaps a difference curve between an exposure curve for a very long time and one for a very short time would give a sensibility curve arising solely from the slow changes in the selenium. However this has not been carefully thought out yet. Observations taken after quickly repeated exposures, particularly to longer wave-lengths, tend to smooth out the maxima. Dr. Pfund has had the kindness to communicate some very interesting and as yet unpublished results by Mr. P. J. Nicholson which are directly in agreement with our result, viz., that the slow rates of change arise from light of the longer wave-lengths. His results show that the form of sensibility curves is markedly altered by varying the wave-length of the preliminary exposure, and that under the continued influence of infra-red radiations (800 μμ), the usual fatigue and lag almost disappear. The, fatigue and lag seem to us merely evidences of the slow changes in conductivity.

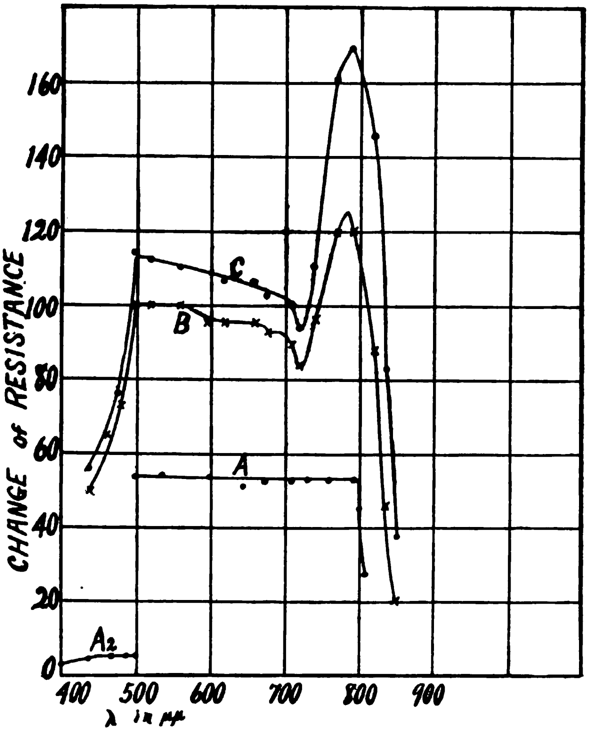

Fig. 3.

A is for 0.4 second exposure; *B* is for 30 seconds exposure; *C* is for 60 seconds exposure.

Having received a more powerful illuminator we are extending our work, to find out the limits in which the change of resistance is independent of the wave-length for short exposure, to establish the law of change of resistance with intensity, and to compare other varieties of selenium and light-sensitive materials.

It is interesting to note how rapidly the curve falls off beyond 800 μμ. We are unable to account for a mechanism that would produce a sudden jump of this kind.

The minima as well as the maxima arise from the longer periods of exposure. It may be that minima indicate the normal states for short exposure for particular wave-lengths, which means that spurious maxima arise from slow changes.

SUMMARY.

1. The sensibility curve for a Giltay cell has been determined under varying conditions.

2. In accordance with theory it has been shown that long periods of exposure give varying degrees of complexity, and are responsible for the regions of maximum sensibility.

3. By long periods of exposure a new maximum is obtained at 800 $\mu\mu$.

4. By exposures of a fraction of a second the maxima and minima vanish and between about 460 $\mu\mu$ and 790 $\mu\mu$ the change of resistance is independent of the wave-length.

5. The work thus far accomplished emphasizes the importance of defining simple conditions for obtaining the maxima of such a complex acting agent as selenium.

6. The maxima and also the minima in the Giltay cell studied arise from the slow rates of change.

7. A selenium cell of this type by virtue of the independence of wave-length for short periods of exposure promises to be the most delicate instrument constructed for measuring energy within the range noted.

THE PHYSICAL LABORATORY,
THE UNIVERSITY OF IOWA.

ON THE NATURE OF THE VOLTA EFFECT; A REPLY.

By Fernando Sanford.

IN the July number of this journal Mr. Albert E. Hennings[1] undertakes to show that the results of an experiment as published by the present writer were spurious. Mr. Hennings bases this charge upon the results of some experiments which he claims "reproduce the essential elements of the experiment described by Sanford." In this claim Mr. Hennings is seriously mistaken, as his experiments reproduce none of the essential elements of the experiment described by me.[2] The experiment which Mr. Hennings undertook to reproduce in a more satisfactory manner was performed by lowering an insulated zinc ball into a hollow conductor until it touched the bottom, then withdrawing it and measuring the contact charge taken by the ball from the inside of the hollow conductor or from a disc of another metal resting upon its bottom. The conclusions drawn from the experiment were based upon the assumption that the metal disc inside the hollow conductor was effectually screened from all outside induction. Mr. Hennings criticized the validity of my conclusions because he thought the metal disc and ball were not screened from the inductive effects of a hypothetical charge on the silk thread by which the ball was insulated.

Mr. Hennings's reproduction of the essential elements of this experiment consists in insulating a metal beaker, then lowering an uninsulated steel ball into it by means of a long conductor connected to earth, withdrawing the long conductor and ball and measuring the contact charge left upon the then insulated beaker.

This arrangement of a metallic beaker connected to earth by a long, uninsulated conductor standing up inside it can be called a hollow conductor only by courtesy, and seems to be especially adapted to eliminating all the properties for which hollow conductors have heretofore been used. The outside of a hollow conductor has been defined as the surface most exposed to the induction of surrounding charges. If this definition be adopted, Mr. Hennings has succeeded in introducing the outside of his hollow conductor into the inside of his beaker. It is at least certain that no experiments in which the shielding properties of a hollow conductor were involved could be performed with such a device as the one invented by Mr. Hennings.

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[1] "Nature of the Volta Effect," Phys. Rev., Ser. II., Vol. I., p. 1.

[2] "On The Nature of the Volta Effect," Phys. Rev., XXXV., 484 (1912).

The remainder of Mr. Hennings's paper contains nothing touching in any way upon the validity of the conclusions drawn from my experiment. In fact, he finally comes to the same conclusion as to the nature of the Volta effect that is stated at the end of my paper. I state as a result of what I conceive to be the teachings of my experiment that "Apparently the Volta effect is not due to any electrolytic action between the opposed metals, but different metals when in contact with the earth or with the inside of the same hollow conductor may be at different potentials relative to each other." Mr. Hennings says, "The surfaces of conductors which have been discharged to earth act just as though they were definitely and characteristically charged."

STANFORD UNIVERSITY,
September 12, 1913

THE MAGNETIC SUSCEPTIBILITY OF GASES.[1]

By W. P. Roop.

1. The explanation of the magnetic properties of substances in terms of electronic motions is the objective point of the physical theory of magnetic phenomena. Recent work has been done in developing a theory of ferro-magnetic phenomena by Weiss and in investigating the magnetic properties of organic compounds by Pascal. In each of these cases, however, the results have been useful principally as determining susceptibility as a function of structural relations rather than as a fundamental property of matter. On the other hand, the theory of Langevin and the magneton hypothesis of Weiss,[2] supported by work at low temperatures in the Leiden laboratory, look toward a more general theory of magnetism, so that magnetic phenomena may be expected eventually to occupy a place in the *electro-magnetisches Weltbild* of Abraham.

It is unfortunate, however, that experimental work has been of necessity almost entirely limited to investigations of the magnetic properties of solids, liquids, and solutions. For it is only in gases that the molecule is sufficiently free from the disturbing influences of its neighbors so that a direct study of molecular properties, as distinguished from structural properties, becomes possible.

2. The study of the magnetic properties of gases is difficult on account of the extreme smallness of the quantities to be measured. This difficulty becomes apparent in the large differences between results obtained by different observers. Oxygen is the only gas whose susceptibility has been measured with sufficient accuracy to justify a comparison of results. Data are also available for air and NO, but the behavior of these is due to the oxygen content. With other gases, there is no agreement, even as to sign. A partial summary of values for the susceptibility of oxygen is given on the following page.

3. Before systematic study of the magnetic properties of gases can be expected to yield valid results, a method must be devised which shall be

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[1] A preliminary report of work conducted under a grant from the Rumford fund of the American Academy of Arts and Sciences.

[2] For a summary of the work of Langevin and Weiss, with references to the papers of the others, see Phys. Ztschrft., 12, 935, 1911.

Observer.	**Mean Value.**	**Mean Error.**	**Reference.**
Quincke....	$.156 \times 10^{-6}$	4.5 per cent.	Ann. d. Ph., 34, 401, 1888.
DuBois.....	.117	....	Ann. d. Ph., 35, 137, 1888.
Hennig.....	.120	1.6 per cent.	Ann. d. Ph., 50, 485, 1893.
Curie......	.167	3.5 per cent.	Ann. Ch. Ph., 5, 289, 1895.
Roop......	.127	5 per cent.	Phys. Ztschrft., 12, 48, 1911.
Piccard.....	.1407	0.1 per cent.	Arch. des Sciences, 35, 480, 1913.

sensitive enough to be used with other gases than oxygen, and which shall give consistent results with oxygen. A suggestion is given by Drude.[1] A manometer consisting of a closed tube containing two fluids (see Fig. 1) becomes very sensitive if the fluids have a small density difference. For ordinary purposes, such a manometer could not be used, since there would be no way of connecting it with the pressure to be measured. But if one of the bounding surfaces be placed in a magnetic field, the surface is displaced into a new equilibrium position such that the hydrostatic pressure due to the displacement is balanced by the pressure due to the magnetic field. The pressure on the bounding surfaces tending to restore them to their equilibrium positions, for a displacement d, is $dg(\rho - \rho_0)$, where ρ and ρ_0 are the respective densities of the fluids. Since there are two such surfaces, each of which is displaced by the same amount, the total pressure tending to restore equilibrium is $2dg(\rho - \rho_0)$. The magnetic pressure tending to disturb the hydrostatic equilibrium is $(\kappa - \kappa_0)/2 \cdot H^2$, where κ and κ_0 are the respective susceptibilities of the two fluids. Equating these pressures, and solving,

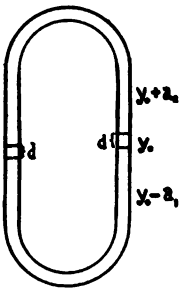

Fig. 1.

$$\kappa - \kappa_0 = \frac{4dg(\rho - \rho_0)}{H^2}.$$

In case the magnetic field intensity H at the other bounding surface is not negligible, this becomes

$$\kappa - \kappa_0 = \frac{4dg(\rho - \rho_0)}{H^2 - H_0^2}.$$

4. Now at the boundary between two gases, there is, of course, no sharp discontinuity. The suggestion of Drude, that a film of liquid be used to separate the gases, seems impracticable. It is possible, however, to carry out the experiment in such a way that the gases only remain in contact with each other for such a short time that diffusion introduces no serious errors.

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[1] Physik des Aethers, 1st ed., p. 148.

Consider the effect of diffusion on a boundary initially sharp. In a straight tube, of uniform bore, the diffusion will be symmetrical, so that the section of the gas column originally constituting the boundary remains the section at which the concentrations of the two gases are equal. In what follows we will designate this section as the boundary. On one side the concentration of one gas, and on the other side the concentration of the other gas, will drop off more or less gradually to zero. Let Y be the coördinate parallel to the axis of the tube. Suppose that the diffusion at a given time t has made the mixture of the gases appreciable to a distance a_1 on one side and a_2 on the other side of the boundary at y_0. The density and susceptibility will vary continuously from $y = y_0 - a_1$ to $y = y_0 + a_2$.

On account of the symmetry of the manometer the hydrostatic force caused by the bodily displacement of both gases, together with the region within which diffusion has occurred, up d cm. on one side, and down the same distance on the other, will be the same as if the boundaries were true discontinuities, provided that the diffusion results in the same distribution of gas on one side as on the other, and does not extend beyond the straight parts of the tube.

As regards the magnetic forces, consider the region between $y_0 - a_1$ and $y_0 + a_2$ to be filled with layers of gas mixture of uniform composition enclosed between cross-sections of the tube at intervals of Δy, differing from each other in composition and susceptibility by differential increments. Denote the concentration of one of the gases at point y by c_y. That of the other is then $1 - c_y$. If susceptibility is an additive function in mixtures, the susceptibility of the mixture at y is $\kappa \cdot c_y + \kappa_0(1 - c_y)$. The susceptibility difference between two neighboring layers is therefore $(\kappa - \kappa_0)\Delta c_y$. The magnetic pressure now becomes

$$\frac{\kappa - \kappa_0}{2} \int_{y_0 - a_1}^{y_0 + a_2} H^2 \cdot \frac{dc_y}{dy} dy.$$

Or, if the limits of integration lie within the region over which H has a sensibly uniform value, we have

$$\frac{\kappa - \kappa_0}{2} H^2 \int_{y_0 - a_1}^{y_0 + a_2} \frac{dc_y}{dy} dy.$$

Since the integral gives the concentration difference between the points $y + a_2$ and $y - a_1$, which is unity, the expression for magnetic pressure reduces to that previously given. The conditions, therefore, under which the simple expression for susceptibility is unchanged by diffusion are these:

(1) Diffusion same on two sides of manometer.
(2) Diffusion limited to straight part of tubes.
(3) Diffusion limited to uniform part of field.
(4) Susceptibility of mixtures additive.

5. Of these conditions, (3) is the most questionable. We may determine approximately the extent to which it is met in the following way. Consider the diffusion in a closed tube of bore negligible relative to the dimensions of the manometer. In such a tube it seems justifiable to assume that diffusion proceeds in such a way as not to disturb the uniformity of concentration in any right section of the tube, so that the concentration gradient remains everywhere parallel to the axis of the tube. Let s be the coördinate measured along this axis. The diffusion proceeds subject to the condition

$$\frac{\partial c}{\partial t} = k\frac{\partial^2 c}{\partial s^2},$$

c being concentration of one of the gases, and k the diffusion constant.

Suppose the tube to be half filled with each of two different gases in such a way that the two boundaries separating the two gases are initially sharp. Consider the origin of the coördinate s to be located half-way between the two boundaries. The initial distribution may then be described as follows:

When $t = 0$,

$$\begin{aligned} c = f_0(s) &= 0 \quad \text{where} \quad -l < s < -\frac{l}{2}, \\ &= 1 \quad \text{where} \quad -\frac{l}{2} < s < +\frac{l}{2}, \\ &= 0 \quad \text{where} \quad +\frac{l}{2} < s < +l. \end{aligned}$$

Here $2l$ is the entire length of the manometer tube, measured along its axis. Further, for all values of t, at the boundaries, where

$$s = \pm\frac{l}{2}, \quad c = \frac{1}{2}.$$

The Fourier series[1]

$$c = q + \Sigma p_n e^{-k\frac{\pi^2 n^2}{l^2}t} \cos\frac{n\pi}{l}s$$

satisfies all conditions if

$$q = \frac{1}{2}$$

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[1] Cf. H. A. Lorentz, Differential- u. Integralrechnung.

and

$$p_n = \frac{1}{l}\int_{-l}^{+l} f_0(s)\cos\frac{n\pi}{l}\,s\,ds$$

$$= (-1)^{\frac{n-1}{2}} \cdot \frac{2}{n\pi} \quad \text{when } n \text{ is odd,}$$

or

$$= 0 \qquad\qquad \text{when } n \text{ is even.}$$

Since the conditions named, viz., the boundary conditions, the initial conditions, and the condition expressed by the differential equation, determine physically the progress of the diffusion, and since the function represented by the Fourier series satisfies all these conditions, this function must give the true relation existing between the concentration, time, and distribution along coördinate *s*. Thus we may determine the extent to which diffusion has caused a failure to meet condition (3) at any time *t*.

6. The method has been tested by the use of a simple apparatus of the form shown in the diagram. The essential part of the apparatus, the gas manometer, is contained between the two three-way cocks, *A* and *B*. One arm of the manometer is placed between the poles of a Weiss electro-magnet,[1] with 10 cm. cores. The other arm is at a distance of 3 cm. from the edge of the cylindrical pole-pieces. One side of the manometer is filled with air, the other with CO_2. On turning the cocks *A* and *B* so as to connect the two sides of the manometer with each other, the heavier gas settles and fills each side of the manometer in the lower half only, while the upper half of each side is occupied by the lighter gas. If now this process is repeated with the magnet acting on the gases on one side, a different position of equilibrium is reached. The distance between these two equilibrium positions is *d*. It is determined by forcing the gas out of each side separately into a gas burette by lifting the mercury reservoir, and measuring the volume of air, after having absorbed the CO_2 in the KOH solution with which the burette is filled and operated. The difference between the volume of unabsorbed gas obtained without the field and that obtained with it,

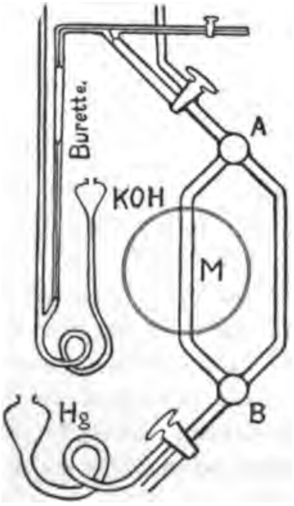

Fig. 2.

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[1] A solenoid cannot be used, both on account of temperature disturbances, and because a manometer of excessively large cross-section would be necessary.

divided by the cross section of the manometer tube, gives d. To calculate d, however, it is only necessary to observe the difference in the burette readings in the two cases, and divide by the ratio of the cross-sectional areas of manometer and burette tubes.

7. The total length $2l$ of the manometer was 50 cm. The internal diameter of the manometer tubes was about 4.5 mm., that of the bore of the cocks being 3 mm. The ratio of cross-sectional areas of manometer and burette tubes was found by mercury weighings to be 11.3. It was found to require about 7 seconds after opening the cocks for the boundaries to reach their equilibrium positions. One cock was in each case opened for that length of time, the other, however, was necessarily open a little longer.

The field was determined by means of a bismuth spiral, using the calibration curve furnished by the makers and correcting for the difference (4°) between the temperature of the calibration and that at which the measurements were made. The current necessary was only 2 amperes (capacity of the magnet 20), and the corrected field intensity was 6,220 gausses. The intensity at the other manometer arm, H_0, was 750 gausses. Whence $H^2 - H_0^2 = 38.2 \times 10^6$.

The mean of six observations of burette reading difference is 4.8 cm., whence $d = .425$ cm. This figure leads to the value of 0.030×10^{-6} for the susceptibility difference between air and CO_2, and to this corresponds a value for the susceptibility of oxygen of 0.144×10^{-6}, that of CO_2 being negligibly small.

By substituting the numerical values for the diffusion constant (0.142 C.G.S.) and the dimensions of the apparatus in the equation obtained in paragraph 5, we find that at the end of 7 seconds the air at a distance of 5 cm. from the boundary contains 7 per cent. of CO_2. Doubtless the diffusion somewhat exceeds the calculated amount, on account of the motion of the boundaries from the cocks to their equilibrium positions. Nevertheless the error due to neglecting diffusion altogether must be small, as the result is close to the average of previously obtained values.

SUMMARY.

A new method for determining gas susceptibility is developed which far exceeds previous methods in sensitiveness.

An illustrative set of data taken with air and CO_2 leads to the value for oxygen of

$$\kappa = 0.144 \times 10^{-6}.$$

CORNELL UNIVERSITY,
July, 1913.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

CONDITIONS INVOLVING A DECREASE OF PRIMARY CURRENT WITH INCREASING SECONDARY CURRENT.[1]

BY F. J. ROGERS.

UNDER all ordinary conditions prevailing in practice an increase of the secondary current in a transformer or induction coil is accompanied by an increase in the primary current. Recently the writer accidentally stumbled upon conditions in which the reverse is true.

A purely experimental investigation showed that the conditions favoring this surprising result were as follows: (1) Small mass of copper in the secondary circuit. (2) High resistance in the primary circuit. (3) Low permeability of the magnetic circuit. When these conditions prevailed in sufficient degree, the secondary could be short-circuited causing a powerful secondary current but accompanied by a *decrease* of the primary current.

By the well-known methods of alternating currents an equation was derived representing the primary current in terms of the impressed E.M.F., the frequency, and the resistances and inductances of the primary and secondary circuits. This was done in the following manner:

Assuming that the impressed E.M.F. in the primary circuit is $E \cos \omega t$, the E.M.F. equations for the two circuits are

$$E \cos \omega t = L_1 \frac{di_1}{dt} + R_1 i_1 - M \frac{di_2}{dt},$$

$$O = L_2 \frac{di_2}{dt} + R_2 i_2 - M \frac{di_1}{dt}.$$

Eliminating the secondary current between these two differential equations and assuming that the primary current is $i = I \cos (\omega t - \theta)$ gives a single equation. This equation can be broken up into two by expanding $\cos (\omega t - \theta)$, collecting the coefficients of $\sin \omega t$ and $\cos \omega t$, and equating each of these coefficients to zero. θ may be eliminated between these two equations thus giving the desired result. If reactances be substituted instead of inductances the equation thus desired, when expressed in its simplest form, becomes:

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 18, 1913.

$$I = \frac{E\sqrt{R_2^2 + x_2^2}}{\sqrt{(R_1x_1 + R_2x_2)^2 + [R_1R_2 - (x_1x_2 - x_{12}^2)]^2}}.$$

I is the primary current and the other symbols have their usual signification, except x_{12} which stands for $2\pi nM$ and may be called *mutual reactance*. When the resistance of the secondary is infinite the above equation reduces to

$$I' = \frac{E}{\sqrt{R_1^2 + x_1^2}}.$$

Multiplying both terms of the fraction by $\sqrt{R_2^2 + x_2^2}$ and simplifying by introducing impedences, our two equations become

$$I = \frac{Ez_2}{\sqrt{(z_1z_2)^2 + x_{12}^2(x_{12}^2 + 2R_1R_2 - 2x_1x_2)}};$$

$$I' = \frac{Ez_2}{\sqrt{(z_1z_2)^2}}.$$

Now it is obvious that the current *I* for a short circuit of the secondary will be less than *I'* if

$$x_{12}^2 + 2R_1R_2 - 2x_1x_2 > 0.$$

In order to verify the formula experimentally a coil was constructed with a primary winding of 1,600 turns of No. 16 and a secondary winding of 200 turns of the same wire. All the constants of this coil were carefully measured. Then a rheostat with known resistances was connected in series with the primary and the primary current was measured both for the secondary open and short-

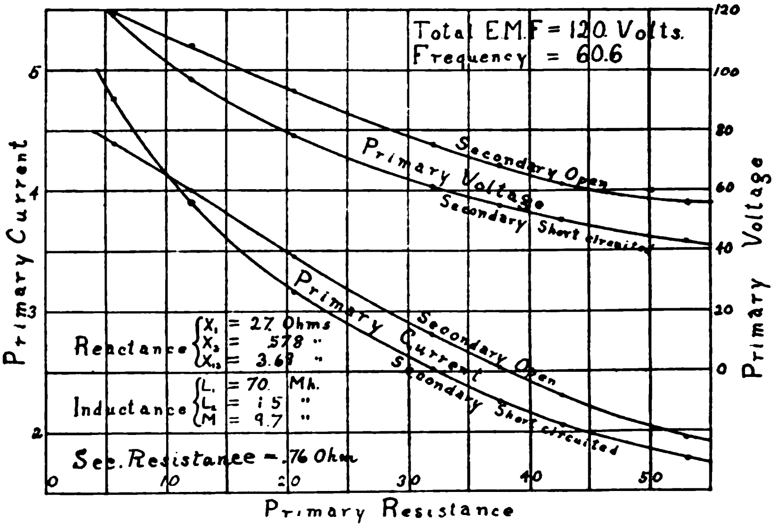

Fig. 1.

circuited. These currents are plotted against the primary resistances in Fig. 1. With the aid of the constants of the coil (also given in the plot) the primary current was computed for each resistance used, according to the equation derived above. In all cases the difference between observed and computed results were within the errors of observation.

After this work had been entirely completed Dr. Bedell kindly called my attention to a paper by E. C. Rimington, Phil. Mag., Vol. 37, p. 394, in which a theoretical treatment of the air core transformer led to a formula equivalent to the one derived above. In a later paper by Bedell, Phil. Mag., Vol. 42, p. 300, a graphical method for studying the increase and decrease of primary impedance when secondary is closed is indicated.

Relativity Theory; General Dynamical Principles.[1]

By Richard C. Tolman.

The Einstein theory of relativity has necessitated a revision of the classical Newtonian mechanics. Some of the consequences have already been presented[2] of a system of mechanics which is based on Newton's three laws of motion,[3] the principle of the conservation of mass, and the Einstein transformation equations for coördinate systems in relative motion. In the article of which this presents an abstract, the writer has derived for a system of particles the important principles of the conservation of momentum and of the conservation of moment of momentum. A further principle has been derived corresponding to that of least action which applies in ordinary mechanics, and this leads to generalized equations of motion in the Lagrangian and Hamiltonian (canonical) forms. We find, however, that the Lagrangian function is *not* to be taken as equal to the difference between the kinetic and potential energies of the system as in the classical mechanics, and the generalized momenta used in the modified Hamiltonian equations are *not* to be defined as the partial differential of the kinetic energy with respect to the generalized velocities as in the older mechanics. In non-Newtonian mechanics the Lagrangian function becomes $L = T - U$, where U is the potential energy of the system and the function $T = \Sigma m_0 c^2(1 - \sqrt{1 - q^2/c^2})$, where m_0 is the mass of a particle at rest, q its velocity, c the velocity of light, and the summation Σ extends over all the particles of the system. The generalized momenta ψ_1, ψ_2, etc., to be used in the Hamiltonian equation of motion are defined in non-Newtonian mechanics by the equations $\psi_1 = \partial T/\partial \dot{\phi}_1$, $\psi_2 = \partial T/\partial \dot{\phi}_2$, etc., where $\dot{\phi}_1$, $\dot{\phi}_2$, etc., are the generalized velocities.

It is hoped that this presentation of the principle of least action and its consequences, in the modified form necessitated by the principle of relativity, will assist in that careful scrutiny which now has to be given to all the results of the older classical mechanics. In the present article the use of the generalized equations has been illustrated by the derivation of a principle corresponding to that of vis-viva in ordinary mechanics. In a following article the ideas here developed will be used in a consideration of the important problem of the equi-partition of energy.

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[1] Abstract presented at the New York meeting of the Physical Society, October 18, 1913.

[2] Lewis and Tolman, Phil. Mag., XVII., p. 510 (1909); Tolman, Phil. Mag., XXI., p. 296 (1911); XXII., p. 458 (1911); XXIII., p. 375 (1912); XXV., p. 150 (1913).

[3] In interpreting the laws of motion we must define force in Newton's original form as equal to the rate of change of momentum instead of in the later form as mass times acceleration, since the two definitions are not identical when the mass changes with the velocity as it does according to the theory of relativity.

This derivation of the principle of least action from the laws of motion is also of particular interest, since writers on relativity[1] have made considerable use of the principle in the fields of pure dynamics, electromagnetics, and thermodynamics, without presenting any derivation in the only field—that of pure dynamics—where such can be obtained.

RELATIVITY THEORY; THE EQUIPARTITION LAW IN A SYSTEM OF PARTICLES.[2]

BY RICHARD C. TOLMAN.

THE principle of relativity necessitates a revision of the kinetic theory of gases. For an ideal gas containing monatomic molecules, all of which have the *same mass*, a modified form of the Maxwell distribution law for the momenta of the molecules has already been derived by Jüttner.[3] In the article, of which this presents an abstract, the writer has considered systems containing particles of *different masses*, and derived also for this case a law for the distribution of momenta. From this distribution law it is shown that the average value of $m_0v^2/\sqrt{1-v^2}$ *is the same for particles of all different masses.*[4]

This equipartition of $(m_0v^2/\sqrt{1-v^2})_{\text{av.}}$ is found true not only for a mixture of particles of different masses, but also for systems of particles which are separated by a partition that allows transfer of energy. Hence the equality of the average values of this quantity becomes the relativity condition for thermal equilibrium. Furthermore, it is shown that $(m_0v^2/\sqrt{1-v^2})_{\text{av.}}$ is proportional to the absolute temperature as measured on the thermodynamic scale, and hence we see that in all such considerations this new quantity satisfies the same relations as the vis-viva m_0v^2 in Newtonian mechanics, and indeed reduces to that quantity when the velocities are small compared with that of light.

We note immediately, however, that the quantity $m_0v^2/\sqrt{1-v^2}$ is neither the relativity expression for the total energy of a particle $m_0\sqrt{1-v^2}$ nor for the kinetic energy $(m_0/\sqrt{1-v^2}) - m_0)$ and hence *in relativity mechanics there can be no possibility of an exact equipartition of energy.* Finally, the writer presents a partial consideration of the actual partition of energy attained at equilibrium.

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[1] Planck, Ann. d. Physik, XXVI., p. 1 (1908); Herglotz, Ann. d. Physik, XXXVI., p. 493 (1911); de Wisniewski, Ann. d. Physik, XL., p. 668 (1913).

[2] Abstract presented at the New York meeting of the Physical Society, October 18, 1913.

[3] Jüttner, Ann. d. Physik, XXXIV., 856 (1911).

[4] v is the ratio of the velocity of the particle to the velocity of light.

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